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NOTES

ON

ELECTROCHEMISTRY

BY

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TO

CHARLES H. SENFF

A TOKEN OF

ESTEEM AND REGARD

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PREFACE.

THE principal aim kept in view in the preparation of these notes has been the giving of a clear and concise presentation of the general principles which underlie electrochemical science.

Endeavor has been made to meet the needs of students entering upon the study of electrochemistry and of chemists interested in the application of electrical energy to chemical problems.

The literature of electrochemistry counts as its own a number of standard works which treat in detail the theories of the science, the methods of electrochemical analysis, and the applications of electrochemistry. Differing from these, the present notes aim merely to offer a general survey of the subject, to serve as an introduction to its study and to aid in the securing of a proper understanding and appreciation of the work along individual lines.

In the chapter on electrotechnology, special endeavor has been made to secure the most recent and reliable data and full advantage has been taken of the information given in leading technical journals and in the excellent monographs of Foerster: Elektrochemie Wässeriger Lösungen, and of Wright: Electric Furnaces and their Industrial Applications.

It must however not be forgotten that exact data of technical operations are often very difficult to procure, and therefore the figures given, while well indicating the general conditions obtaining, cannot in all cases claim to be actual working formulæ.

Prefacing each chapter there will be found a bibliography

61,624

of important treatises bearing upon the subject-matter discussed in the chapter. The works so indicated have all been consulted in the preparation of these pages, and the writer would here take opportunity to express his obligations to their authors.

F. G. W.

TABLE OF CONTENTS.

PREFACE v

CHAPTER I. GENERAL PRINCIPLES. 1

General Principles of Science — Matter and Energy — Forms of Energy — Measurement of Physical Phenomena.

CHAPTER II. ELECTRICAL ENERGY 8

Theories of Electricity — Radio-activity — Factors of Electrical Energy — Properties of Electricity — Ohm's Law.

CHAPTER III. ELECTROCHEMISTRY 22

Evolution of Electrochemistry — Electrolysis — Electromotive Force — Dissociation Voltage.

CHAPTER IV. ELECTROLYTIC DISSOCIATION 41

The Ion Theory — Conductivity — Migration of Ions.

CHAPTER V. ELECTRO-ANALYSIS 66

Electro-analysis — Reversible Reactions and Cells — Sources of Current — Current Measurement — Current Regulation — Electrodes — Currrent Density — Records — Resumé.

CHAPTER VI. ELECTROTECHNOLOGY 93

Introduction — Direct Action Processes : Electrodeposition from Solution — Electroplating — Chlorine and Alkali Hydrates — Indirect Action Processes : Electrodeposition from Fused Electrolytes — Electrothermic Processes : Electro-furnaces — Electro-furnace Products — Electro-Organic Processes : Direct Action Processes — Silent Discharge — Electro-Osmosis.

NAME INDEX 139

SUBJECT INDEX 141

NOTES ON ELECTROCHEMISTRY.

CHAPTER I.

GENERAL PRINCIPLES.

Literature: HERING, C.: "Ready Reference Tables," Vol. I. New York, 1904. HOLMAN, S. W.: "Matter, Energy, Force, and Work." New York, 1898. NOYES, A. A.: "General Principles of Physical Science." New York, 1902. WHETHAM, W. C. D.: "The Recent Development of Physical Science." Philadelphia, 1904.

General Principles of Science. — Before taking up for consideration the subject to which these notes are to be devoted, it will not prove amiss to refer briefly to some of the general principles which underlie electrochemistry, as they do all branches of physical science.

Science is defined as systematized knowledge. Physical science, in its broader aspect, may be said to deal with all phenomena of nature, the Greek word, *physis*, signifying all nature. Physical science, then, seeks to give a thorough presentation of all natural phenomena, and to formulate principles which will permit of the prediction of such phenomena.

There are two methods which may be legitimately followed in scientific investigation, — experience, and speculation based on experience. These two methods are mutually supplementary and interdependent, for, reduced to final terms, all human science is knowledge based on experience.

The first step to be taken in experimental investigation is the collection and accumulation of facts. When a sufficient number of data have been secured, the more the better, the

proper grouping and correlation of these data are required. This is achieved by the process of inductive reasoning.

Induction consists in the drawing of conclusions from observed facts, in the inference of general principles from the consideration of individual cases.

But it is not always possible to apply the inductive method, owing to the great number and the complexity of natural phenomena, and, therefore, recourse is often had to another method of reasoning, — deduction.

Deduction consists in the advancing of some general supposition provisionally adopted to account for certain phenomena, and then submitting such supposition to the test of experiment.

All suppositions of this kind are termed hypotheses. An hypothesis is, therefore, merely a tentative conjecture as to the nature and cause of phenomena. All logical deductions drawn from an hypothesis, unless supported by experimental demonstration, are called theories.

The crucial test as to the value and validity of all hypotheses and theories is, of course, their concordance with results obtained by experiment. Discovery of any fact or facts not in agreement with the tenets of a given hypothesis or theory, at once forces the modification or even abandonment of the theory.

Deduction, then, consists in the derivation of specific conclusions from a more general proposition; it is obviously the inverse of induction.

When a general theory, evolved by either the inductive or the deductive method, has been submitted to and verified by experimental proof, it is termed a law.

A law must not only embrace all known facts and phenomena to which it refers, but must also be able to account for all phenomena of like character which may ever be discovered. In fact, a law must, to a certain extent, be capable of predicting such phenomena.

A law is simply a concise expression of the results of experience. As Whetham has so ably expressed it: "We must look upon natural laws merely as convenient shorthand statements of the organized information that is at present at our disposal."

Matter and Energy. — Matter and energy are primary concepts employed to simplify and to systematize our impressions of natural phenomena.

The two fundamental laws of physical science are concerned with these concepts. These laws are the law of the conservation of matter, due to Lavoisier, 1789, and the law of the conservation of energy, due to Robert Mayer, 1842. The first of these laws holds that matter, the second, that energy, can be neither created nor destroyed.

If we are willing to accept an inseparable blending of matter and energy, giving to this concept the designation, substance, then both of the laws given may be incorporated as one, the law of substance: Substance can be neither created nor destroyed. This law of substance is — as far as human reason can conceive — a law of universal validity, a law of the cosmos.

Viewed as a component of substance, matter must be regarded as its inert constituent; it may be defined as that which has extension, which occupies space, which constitutes the tangible portion of the universe.

Energy, the other component of substance, may be considered as the cause of all changes, of all physical phenomena. As Maxwell has expressed it: "Energy . . . that which in all natural phenomena is continually passing from one portion of matter to another. Energy cannot exist except in connection with matter."

The term "energy" was first introduced by Young, in 1832, as a designation of the product mv^2 (*vis viva*); in the sense in which it is now commonly accepted, it has been used since about 1860.

The principle of the conservation of energy, or, the first law of energetics as it is sometimes called, was first formulated by Robert Mayer as a broad generalization from experimental evidence. About 1842 Joule furnished much direct and valuable experimental testimony of its truth, and every test ever made of this most important law has affirmed its correctness.

Forms of Energy. — Energy appears in various forms, for instance as mechanical, as thermal, as chemical, and as electrical energy. These forms are mutually convertible, and whenever a given quantity of some one kind of energy disappears, an exactly equivalent amount of some one other or of several other kinds of energy appear.

There is, however, one limitation that must be noted in this connection. Whereas all forms of energy can be transformed into thermal energy, the complete changing of thermal energy into mechanical, or into other forms of energy, cannot be effected. This principle is known as the second law of energetics.

All forms of energy may be regarded as the product of two factors, intensity and capacity. The former determines whether the energy in a given system must be active or at rest; the capacity-factor determines the quantity of energy present in a given system. In all energy transformations a part of the original energy is changed into heat, and thus, eventually, all energy is doomed to pass into this form; at least at present no process working to reverse this outcome is known.

Furthermore, in all transformations of heat-energy a part of this energy passes to a lower temperature; radiation, conduction, and convection aiding to bring about this result. Temperature, however, is the intensity-factor of thermal energy, and, as no work can be obtained from heat unless there are differences in temperature, ultimately, it seems, all energy must pass into the form of diffused heat. When

this shall have occurred, the universe will have attained to one and the same temperature, and then all life and motion must come to an end. This doctrine, known as the theory of the dissipation or the degradation of energy, was first suggested by Sir William Thomson (Lord Kelvin).

Measurement of Physical Phenomena. — Besides matter and energy there are two fundamental concepts which enter into the contemplation of every physical phenomenon where a quantitative study of the same is attempted. These concepts are time and space. Time may be considered as a recognition of sequence in human consciousness. The simplest form of the concept of space is length.

Time, space, and mass are of primary importance in nearly all measurements of physical phenomena. To effect such measurements it is necessary to establish a system of standards to which these measurements can be referred. Various systems of standards have been devised; they differ from one another principally in the selection of their fundamental units. As a matter of fact, however, there is practically only one system used in the scientific work of to-day. This is the centimeter-gram-second system, the C.G.S. system, as it is generally termed from the initial letters of its three units of space, mass, and time.

The unit of length adopted in this system is the centimeter. This is the one-hundredth part of the standard meter, a bar made of an alloy consisting of 90% platinum and of 10% iridium. This standard bar is preserved by the International Bureau of Weights and Measures in Sèvres, near Paris, France.

The unit of mass * of the C.G.S. system is the mass of one

* Conception of mass, as this term is now used, is due to Newton. A clear distinction must be made between mass and weight. The mass of a body is invariable; it is the same throughout the universe. The weight of a body depends on gravitation: on the earth, for instance, the weight of a body measures the earth's attraction for that

cubic centimeter of water at a temperature of 4° Centigrade. It is represented by the one-thousandth part of the International kilogram, a cylinder made of the same alloy of which the standard meter is made; it also is preserved by the International Bureau of Weights and Measures in France. Copies of these International standards are in the possession of the United States Government at Washington, D.C.

The unit of time of the C.G.S. system is the solar second. This is the $\frac{1}{86400}$ part of a mean solar day. The duration of the latter is of course determined by the motion of the earth with respect to the sun, the interval between successive transits of the sun over the meridian.

All of the fundamental quantities used in the C.G.S. system are fixed and unvariable; and as definite amounts of these quantities, the centimeter, the gram, and the second, have been accepted, this C.G.S. system is designated as an *absolute* system of units.

The unit of velocity adopted in this system is one centimeter per second. The unit of force, that force which, acting on one gram-mass at rest, produces in one second a velocity of one centimeter per second — this is called a dyne. The unit of energy is the erg: an erg is one dyne acting through one centimeter.

The units of all forms of energy can be referred to the centimeter, the gram, and the second. In the measurement of electrical energy there are two C.G.S. systems: the electrostatic and the electromagnetic system. In the electrostatic system all units are based upon the force exerted between two quantities of electricity — that amount of electricity which attracts or repels an equal amount of electricity one centimeter distant with the force of one dyne.

body. Weight, however, is the most convenient measure of mass, and consequently these two terms are frequently, though erroneously, considered synonymous.

The electromagnetic system is based upon the force exerted between an electric current and a magnetic pole. In this system the unit current of electricity is defined as that current which, flowing through an arc of one centimeter, curved to a radius of one centimeter, generates a unit magnetic pole at the center. The electrical units in common use are based on this system.

CHAPTER II.

ELECTRICAL ENERGY.

Literature: Deschanel, A. P., and Everett, J. D.: "Natural Philosophy." New York, 1889. Haber, F.: "Grundriss der Technischen Elektrochemie auf Theoretischer Grundlage." München, 1898. Hering, C.: "Ready Reference Tables," Vol. I. New York, 1904. Le Blanc, M. (English translation by Whitney, W. R.): "Elements of Electrochemistry." London, 1896. Rosenberg, E. (English translation by See, W. W. H., and Kinzbrunner, C.): "Electrical Engineering." New York, 1903. Rutherford, E: "Radio-Activity." Cambridge, 1904. Soddy, F.: "Radio-Activity, an Elementary Treatise, from the Standpoint of the Disintegration Theory." New York, 1904.

Theories of Electricity. — The word "electricity" is derived from the Greek, *electron*, amber, because the manifestation of certain electrical properties — attraction, repulsion — was originally noted in amber. Credit for having been the first to observe these phenomena is generally given to Thales, who lived some two thousand years ago.

Introduction of the word "electricity" is due to William Gilbert, or Gilberd (1540–1603), who has been named "the creator of the science of electricity." His principal work, "De Magnete, Magneticisque Corporibus, et de Magno Magnete Tellure, Physiologia Nova," published in 1600, is replete with interesting facts and observations of magnetic phenomena.

Since the days of Gilbert innumerable observations of electrical phenomena have been made, and a great number of data bearing on them have been recorded. Still, although so much is known of the properties of electricity, and although electricity has unquestionably become one of the

most potent agencies in the advancement of human welfare, the true nature of electricity remains as yet an unsolved problem.

At various times, various theories have been advanced in explanation of electrical phenomena. Thus, Benjamin Franklin (1706–1790) suggested the one-fluid theory of electricity. All unelectrified bodies were supposed to possess a normal amount of electricity; a positively electrified body contained an excess, a negatively electrified body, a deficiency of this electric fluid.

Franklin was the one to introduce the terms positive and negative electricity. They are retained to this day as conventional terms, indicating for one thing forces in opposite directions, — for instance, the direction of flow of electric currents.

Dufaye, in 1733, originally advanced the two-fluid theory of electricity; it was more precisely formulated by Symmer. This theory holds that there are two kinds of electricity — positive and negative; union of equal amounts of the two forms the neutral fluid, which is present in all unelectrified bodies. The total amount of electric fluid in a body is a constant quantity; additional gain of the one kind necessitates an equivalent loss of the other. Whenever an electric current of one kind flows through a conductor in one direction, an equivalent amount of current of the other kind flows in the opposite direction.

Both of these "fluid" theories hold in common that the electricity passing along a conductor — the electric current — is continuous in character.

Recent studies, however, made in the discharge of electricity through gases, have brought about a decided change of view concerning the nature of electricity.

Such discharges of electricity through gases are unquestionably convective. Particles charged with positive, and particles charged with negative electricity, are present in gases;

these particles, ions, which term signifies wanderers, can be induced in gases by Röntgen rays, by ultra-violet light, and by other means. They move under the influence of electrical energy, and it is their motion which constitutes the electric current.

From the researches of J. J. Thomson it appears that the negatively charged particles thus present in a gas have a mass of approximately one one-thousandth that of a hydrogen atom; positively charged particles of similar dimensions are not known.

The electron theory, the theory which promises to become the leading theory of electricity in the immediate future, is based on these studies. According to the electron theory there exists but one kind of electricity, — that which is generally designated as negative electricity.

This negative electricity is assumed to occur in definite unit charges, and these smallest particles of electricity, the atoms of electricity, are termed electrons.

The term "electron" was originally given by G. Johnstone Stoney to the definite charges of electricity associated with ions; the concept of electrons as separate, distinct individual particles was only arrived at later. However, in this connection it is interesting to recall that W. K. Clifford, as early as 1875, made the following statement: "There is great reason to believe that every material atom carries upon it a small electric current, if it does not wholly consist of this current."

In a substance which is electrically neutral, the electrons are so disposed with respect to the balance of the matter that there is no evidence of an outside electric field.

In a substance which bears a positive charge of electricity, there is a lack, a deficiency of electrons. A substance which is negatively charged has an excess of electrons. As Sir William Crookes has expressed it: "A so-called negatively charged chemical atom is one having a surplus of electrons, the number depending on the valency, whilst a positive ion

is one having a deficiency of electrons. Differences of electrical charge may thus be likened to debits and credits in one's banking account, the electrons acting as current coin of the realm. On this view only the electron exists; it is the atom of electricity, and the words positive and negative, signifying defect and excess * of electrons, are only used for convenience of old-fashioned nomenclature."

Radio-Activity. — In this connection reference must be had to the subject of radio-activity, a theme so intimately concerned with the theory of electrons, and of vital interest and importance on account of the far-reaching influence it is exerting on the present trend of physical science in particular, and of scientific thought in general.

Discovery of the *X*-rays by Röntgen (1895) led to numerous researches to determine whether analogous radiations might not be given out by other substances. Thus, Becquerel, in 1896, discovered the radio-activity of uranium; G. C. Schmidt, in 1898, that of thorium; and M. and Mme. Curie, together with M. Bémont, also in the year last named, isolated the new element radium from the mineral pitchblende.

Radium gives out three kinds of rays, named the α-, β-, and γ-rays.

The α-rays are material particles bearing charges of positive electricity. They have a mass equal to about twice the mass of a hydrogen atom; they move with a velocity about one-tenth that of light, *i.e.*, about 20,000 miles per second, and are readily arrested by an air-gap of a few centimeters, by paper, and by thin layers of aluminium foil. The luminous phenomena shown by the spinthariscope of Sir William Crookes are caused by the impact of α- particles on a screen of sulphide of zinc, these impacts of the swiftly moving par-

* In the original, Bericht V. Int. Kong. Ang. Chem. 1903, Vol. I, p. 96, the words "defect" and "excess" are printed in reverse order. — F. G. W.

ticles evoking the flashes which make the screen appear a seething sea of light.

The β-rays are in all probability identical with the cathode rays which appear at the negative electrode of a vacuum tube on the passing of an electric discharge. These β-rays consist of negatively charged particles having a mass of approximately one one-thousandth the mass of a hydrogen atom; they travel with a velocity approximating to that of light. The minuteness of these little particles will be appreciated from a comparison made by Sir William Crookes, who stated, that if the sun's diameter were taken to be about one and one-half million kilometers, and that of the smallest planetoid about twenty-four kilometers, that then, if an atom of hydrogen were magnified to the size of the sun, an electron would have a diameter about two-thirds that of the planetoid.

The β-rays are the chief agents in the photo-activity of the radium rays. Like the α-rays, the β-rays are also deflected by a magnetic field, but in a direction opposite to that in which the α-rays are turned.

The γ-rays are more penetrating than either the α- or β-rays. They are not deflected by an electric field, and thus far no proof has been furnished that they are material particles; possibly they may be ethereal vibrations analogous to, or even identical with, the Röntgen rays.

Considered as a whole, radium rays exercise certain remarkable influences. They evoke luminosity in some substances, in sulphide of zinc, for instance, and in diamonds; they destroy the power of germination in seeds; they can extend the larvae stage of some insects, and can cause burns and even bring death to living organisms.

The property which radium rays possess of ionizing dry air and other gases, that is, of making these substances conductors of electricity, is taken advantage of for their detection and for the measurement of the strength of radium preparations. This determination is accomplished by bring-

ing a sealed tube containing radium into the neighborhood of an aluminium-foil electroscope placed in dry air. The radium transforms the air, which is normally an insulator, into a conductor, and this enables the electric charge of the electroscope to pass away. The speed with which this discharge takes place allows of a quantitative estimation of the radio-activity of the preparation.

In addition to the three kinds of rays which radium emits, it also gives off an emanation which is more radio-active than radium itself. This emanation is poisonous to animal life, is very unstable, slightly soluble in water, and is condensed at a temperature of — 150° C. to — 155° C.

As determined by Sir William Ramsay and Mr. Soddy, this emanation has been found to yield another element — helium — as one of its products of decomposition. Apparently, radium passes through six other stages before it finally appears in the form of helium, which is *not* radio-active. This transformation proceeds undisturbed by changes in external conditions, such as changes in temperature, light, or darkness. It has been estimated that about one two-thousandth part of a given quantity of pure radium disintegrates per annum. The change of radium into helium is thus far the only authenticated instance known of a transmutation of one element into another.

Induced radio-activity is caused by a very fine film of a solid substance deposited by the radium emanation on surfaces exposed to it. This film may be mechanically removed by brushing or by wiping it with a cloth; if left undisturbed this film soon loses its radio-activity.

Radium also continuously gives out energy in the form of heat. One gram of pure radium gives out about 100 calories per hour, and Rutherford has estimated that the heat given out by the transformation of one gram of radium into helium is about one million times as great as the heat given out in the formation of one gram of water.

An interesting hypothesis to account for the usual positive electrification of the atmosphere and for the negative electrification of the earth, has been based by Professor Ebert on the activity of radio-emanations. He holds that these emanations in passing from the earth into the atmosphere impart their negative charge to the capillaries of the soil through which they pass, and thus enter the air with high positive charges, which they transmit to the atmosphere.

Factors of Electrical Energy. — If one chooses to look upon electricity as a form of energy, then electricity, like all other forms of energy, may be viewed as the product of two factors, — an intensity-factor and a capacity-factor.

The intensity-factor of electrical energy is termed its potential or tension; the capacity-factor represents quantity of electricity. To compare electrical with thermal energy, for instance, electric potential corresponds to the temperature of thermal energy, electric capacity corresponds to heat-capacity.

Heat always passes from objects of a higher to objects of a lower temperature; the extent of heat-exchange between two points of unequal temperatures is determined solely by the difference between those temperatures, but is wholly independent of the absolute temperatures.

In a similar manner the passing of an electric current between two points is determined by the difference in tension-potential between those points. When positive electricity passes from a point of higher to a lower potential, a corresponding amount of negative electricity must be conceived of as passing in the opposite direction. This may, in a way, be regarded as analogous to the conception that a given amount of cold is raised to a higher temperature whenever an equal amount of heat passes from a higher to a lower temperature.

Properties of Electricity. — Electricity may be conveyed from one location to another either by means of conductors

in which there is no evident, simultaneous movement of the matter of which the conductor consists, or by means of substances in which a transportation of material particles accompanies the transference of the electric charge. Conductors of the former kind are known as conductors of the first class; the metals, metallic sulphides, and carbon belong to this group. Conductors of the other kind are called conductors of the second class; to these belong the salts, the acids and bases when in solution, and salts and bases also when in a state of fusion.

While the domain of electrochemistry lies essentially with conductors of the second class, for the moment attention shall be given to the phenomena to be noted when a current of electricity flows along a conductor of the first class, for instance, along a metal wire.

If a plate of copper and a plate of zinc are placed in a vessel containing dilute sulphuric acid, and the two metal plates are connected by a metal wire, outside of the fluid, observation will show that this wire soon becomes heated, and if a break is made anywhere in this wire so that an air-gap intervenes between the two ends of the wire, a spark of light will appear the instant the break is made.

If the wire remain unbroken, a magnetic needle brought near to it will be deflected from its normal position. If the wire be wound around a bar of soft iron, the iron becomes magnetic, and remains so at least as long as the wire encircles it. If the wire be cut or broken and the ends inserted in acidulated water, bubbles will arise from the water, and the water will be found to suffer decomposition into its component elements, oxygen and hydrogen gases.

These phenomena make evident that some process is taking place — an electric current is passing along the wire, and the phenomena referred to establish the fact that an electric current can induce heating, lighting, magnetic and chemical effects.

There is evidently a force at work which drives the electric current along the wire. If we use two galvanic elements instead of one, connecting the zinc-plate of element No. 1 with the copper-plate of element No. 2, and then lead a connecting wire from the copper-plate of No. 1 to the zinc-plate of No. 2, a much stronger current will be secured than if only one element had been used. It appears that the pressure driving the electric current along the wire has been increased. The pressure thus forcing the current along the wire is termed electromotive force, and the unit in terms of which this is measured is the volt.

The International volt is that electromotive force which will maintain one International ampere through a resistance of one International ohm. For practical purposes it is represented by $1 \div 1.434$ of that of a Clark cell at 15° C.

The cause of the flow of the electric current is, as has been said, a difference in the electrical pressure, a difference in electrical potential between different parts of the circuit. Water standing in two connecting vessels will remain at rest whenever it stands at the same level in both vessels. If, however, there is a difference of level in the two vessels, then the force determined by the difference in height of these levels will cause a current of water to flow from the higher to the lower level. By analogy we can conceive a similar difference in electric pressure to be the cause of flow of an electric current.

The rate of flow of an electric current per second is termed its current strength. Current strength, or current intensity, as it is also called, is measured in amperes. The International ampere is the current which, under specified conditions, will deposit 0.001118 gram of silver per second.

Amperes are comparable to the flow of water measured in some unit of volume, for instance, in liters or in cubic feet per second. Thus, a flow of water of 20 liters per second under a pressure of 50 kilograms, increases to a flow of 40

liters per second under a pressure of 100 kilograms. In an analogous manner an electric current of 20 amperes under an electric pressure of 50 volts is changed to a current of 40 amperes under a pressure of 100 volts. Amperes do not decrease by doing work, neither does a volume of water grow less in consequence of doing work, driving a turbine, for instance; the work done is in direct ratio to the drop in potential or pressure.

In passing through a conductor, the electric current has to overcome the resistance in its path. The longer the conductor, a wire, for instance, and the smaller its cross-section, the greater is the resistance to be overcome. In other words, it may be said that the resistance varies directly as the length and inversely as the cross-section of the conductor along which a current flows.

Resistance is measured in units called ohms. The International ohm is represented by the resistance of a column of mercury at 0° C. 106.3 centimeters long, weighing 14.4521 grams, and having a uniform cross-section. The resistance met by an electric current in its flow is directly comparable to the friction encountered by a current of water flowing through a pipe; there, too, the friction varies directly with the length of the pipe and inversely with its diameter.

The names of the electrical units thus far considered are derived from the names of men eminent in the development of electrical science. Thus, the volt is taken from the name of Alexander Volta (1745–1827), the ampere from that of André Marie Ampere (1775–1836), the ohm from that of Georg Simon Ohm (1789–1854).

Ohm's Law. — There is an intimate relation between the electromotive force, the current strength, and the resistance of an electric current.

If these terms be represented by their initial letters, thus:

Current strength $= C$,
Electromotive force $= E$,
Resistance $= R$,

the expression $C = \frac{E}{R}$ indicates that the current strength is equal to the electromotive force divided by the resistance.

This is the famous law of Ohm, the discoverer of the relation here expressed; it is a law of fundamental importance in electrical science.

By transposition we have:

$$C = \frac{E}{R},$$

$$R = \frac{E}{C},$$

$$E = CR,$$

and as the unit of current strength is the ampere, that of resistance the ohm, and that of electromotive force the volt, these formulæ express that:

Amperes = volts $\div$ ohms,
Ohms = volts $\div$ amperes,
Volts = amperes $\times$ ohms.

In addition to the units discussed, there are several others which are frequently used in considering electrical data.

The coulomb is the unit of electrical quantity; the word is derived from the name of Charles Augustin Coulomb (1736–1806). The International coulomb is defined as the quantity of electricity transferred by a current of one International ampere in one second.

Sometimes the quantity of electricity transferred by a current of one ampere in one hour is employed as a unit; this is called an ampere-hour, and is a unit much used in electrochemistry.

The farad, derived from the name of Michael Faraday (1791–1867), is the unit of electrical capacity, for instance, of a condenser, to hold electric charges under electric pressure or stress. The capacity in farads equals the charge in coulombs divided by the electromotive force in volts. The unit actually used, however, for measurements of electrical capacity, is the microfarad, one one-millionth of a farad.

The watt is the unit of electrical power; the name commemorates James Watt (1736–1819), the pioneer of modern steam-engineering. The power in watts is the product obtained by multiplying volts and amperes. Representing power by P, the various relations between power, electromotive force, current strength, and resistance are indicated by the formulæ: $P = EC$; $P = \frac{E^2}{R}$; $P = C^2R$. The dependence of electric power on both current strength and voltage is evident from a consideration of the analogy previously introduced. In that case, it will be recalled, the work effected by the flowing water was determined by both the difference in height between the two water-levels and by the amount of water passed. One kilogram of water flowing down a height of one hundred meters, will do five times the work that is done by one kilogram of water flowing down a height of twenty meters. The power of falling water is thus measured in kilogrammeters per unit of time (second or minute); 75.0 kilogrammeters per second are one metric horse-power. The flow of water per second corresponds to the electric current strength; the water-pressure due to the difference of the water-levels, to its voltage. Thus, 735.448 watts are equal to one metric horse-power. One thousand watts are called one kilowatt, and are equivalent to 1.35972 metric horse-powers.*

* 1 H.P. = 76.0404 kg.-meters per second.
1 H.P. = 745.650 watts.
1.34111 H.P. = 1000 watts.

The unit of electrical energy or work is the joule. The term is derived from the name of James Prescott Joule (1818–1889), who practically prepared the way for the scientific study of thermodynamics.

A current of one International ampere flowing through a resistance of one International ohm for one second does one joule of work. Joules are the product of coulombs and volts; in other words, joules represent watts per second.

If the ampere-hour is taken as the unit of electrical quantity, the corresponding unit of electrical energy or work is the volt-ampere-hour; this is generally designated as the watt-hour; 1000 watt-hours are termed one kilowatt-hour.

The relation between electrical energy and heat energy was clearly established by Joule, in 1841. This relation is expressed in the following law which bears his name: "The heat generated in the whole or in a part of an electric circuit in the unit of time, is proportional to the resistance and to the square of the current strength."

Experimental study has shown that 4.18617 (approximately, 4.2) watts per second correspond to 1 calorie — the calorie being defined as the amount of heat necessary to raise the temperature of one gram of water from 15° to 16° hydrogen scale. This is regarded as equivalent to one one-hundredth of the amount of heat that will raise the temperature of one gram of water from 0° to 100° C. $1 \div 4.18617 = 0.238882$; therefore 0.238882 calorie is the heat equivalent of one joule, and this means that one joule will raise the temperature of 0.238882 gram of water 1° C.

The unit of inductance is the henry, named for Joseph Henry (1797–1878). This unit is used in measuring the intensity of that property in virtue of which changes of current in the circuit itself, or changes of current in an adjacent circuit, produce electromotive force. The henry is the quotient obtained by dividing induced volts by rate of change of amperes per second.

The values of the various electrical units discussed were fixed by an International Congress of Electricians, which met in Chicago, United States of America, in 1893.

It will be recalled that the absolute system of electrical units used is electromagnetic in character; that is to say, that the units in that system are based upon the force exerted between an electric current and a magnetic pole. As these regular C.G.S. units are, however, as a rule either too great or too small for convenient practical use, the system of practical units, which has just been so fully discussed, has been devised.

These practical units, as they are called, are either exact multiples or submultiples of the absolute C.G.S. units of the electromagnetic system. The following table shows their relation:

Unit of:	Name:	Corresponds to C.G.S., Units: *
Electromotive-force	Volt	10^8
Current strength	Ampere	10^{-1}
Resistance	Ohm	10^9
Quantity	Coulomb	10^{-1}
Capacity	Farad	10^{-9}
Power	Watt	10^7 erg per second
Energy or Work	Joule	10^7 erg
Inductance	Henry	10^9

* In index-notation a positive exponent indicates an integral number; thus, $10^2 = 100$, $10^3 = 1000$, etc. A negative exponent denotes the reciprocal of the indicated power of 10; thus, $10^{-2} = 0.01$, $10^{-3} = 0.001$, etc. . . .

CHAPTER III.

ELECTROCHEMISTRY.

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Evolution of Electrochemistry. — Electrochemistry is the study of the mutual relation and transmutation of electrical and chemical energy. It deals with electrical phenomena which are caused by chemical reactions, and with chemical changes which result from the application of electrical energy.

Perhaps the earliest instance on record of the bringing about of chemical change by electricity is the reduction of metallic zinc and mercury from their respective oxides by Beccaria, about the seventh decade of the eighteenth century, who achieved his results by sparking the oxides of the metals named by discharges from Leyden jars.

In 1775 John Priestley discovered that electric sparks passing through air acidify the air. Priestley believed that the acid produced was carbonic acid, but Cavendish, repeating the experiments of Priestley, showed that nitrous and nitric acids were formed.

Ten years later Van Marum in Rotterdam, subjected many

gases and metallic substances to the discharges of a powerful electrical friction machine, and among other chemical changes which he thus effected was the decomposition of "alkaline air" (ammonia) into its components, nitrogen and hydrogen.

Electrolytic decomposition of water into "combustible air" (hydrogen) and "life air" (oxygen) was accomplished, in 1789, by Paets van Troostwijk, Deimann, and Cuthbertson. Their experiments were most carefully made with distilled water and with water from which the absorbed air had been removed under vacuum; they thus proved the belief that water consists of hydrogen and oxygen gases to be well founded.

The speculations which were indulged in at that time regarding the nature of electricity are interesting. By some, electricity was held to be a substance dual in its character, which entered into union with the elemental constituents of the compounds decomposed by its influence; others believed it to be a highly concentrated form of fire and accounted for its great powers on that supposition.

The experiments so far referred to, all relate to the production of chemical effects by the agency of electrical energy. The first attempt recorded to produce electrical phenomena by chemical agencies is the experiment made by Alessandro Volta, Lavoisier, and De Laplace, which consisted in electrifying an isolated metallic plate by placing on it, respectively, basins with burning charcoal and dishes in which sulphuric acid was poured over iron filings.

About the same time, in 1782, these investigators attempted, although with but indifferent success, to generate electricity by the evaporation of water and the subsequent condensation of the vapor, Volta having been led to the conception of this idea through his studies of atmospheric electricity, in which he had noticed indications of the presence of electric charges in rain and in fog.

An incidental observation made during some physiological experiments led Aloysius Galvani, professor at the University of Bologna, in 1791, to the discovery of a form of electricity until then unknown; he styled it animal electricity, concluding that the electricity thus made manifest in his experiments was produced by the brain of the animals on which he worked, and that the electricity thus segregated from the blood passed through the nerve-channels into the muscles, these being practically a kind of Leyden jar.

Volta, although he originally shared the views of Galvani, was gradually led to abandon the supposed biological origin of these electrical manifestations, and ultimately showed their origin to lie in the contact of two dissimilar metals. This discovery led him to establish the contact theory of electricity, 1792–1793, which held sway for many years.

In 1800 Volta published an account of the voltaic pile, which made it possible to produce galvanic electricity — "metallic electricity," as Volta termed it — in sufficient quantity and of sufficiently high potential to permit of a study of chemical actions induced by the electric current. The beginning of electrochemistry proper may, therefore, be said to date from the invention of the voltaic pile, although it should not be forgotten that Professor Fabroni, of Florence, in 1792, had suggested chemical action to be "the nature of the new stimulus," in speaking of electricity evoked by the immersion of metals in water.

In 1800, the same year in which Volta announced the construction of the voltaic pile, Carlisle and Nicholson effected the electrolytic decomposition of water by means of such a pile, an experiment which, it will be recalled, had already been made by the aid of frictional electricity in 1789. Carlisle and Nicholson also noticed the chemical reactions taking place within the voltaic pile itself. A little later Dr. Henry, of Manchester, England, effected the electrolytic decomposition of ammonia, of nitric acid, and of sulphuric acid.

Dr. Wollaston, in 1801, ascertained that silver can be electrolytically plated with copper, if the silver, in connection with some metal more positive than itself, is immersed in a solution of a copper salt. In 1803 Berzelius and Hissinger effected the electrolytic decomposition of water and of some neutral salts, while about the same time Cruickshank suggested the use of the electric current for the analysis of minerals, he having observed the electro-deposition of silver, copper, and lead from some of their respective salts. In 1805 the electro-deposition of gold on silver, and the electro-deposition of zinc were discovered by Brugnatelli.

In this same year Von Grothuss offered an explanation to account for the electrolytic decomposition of water. At the instant of such decomposition of a molecule of water, the hydrogen is charged electropositively and the oxygen electronegatively. The former is repelled from the positive pole and is attracted to the negative pole; the oxygen is repelled from the negative, and is attracted to the positive pole. The initial work the electricity was supposed to perform was decomposition of the water molecules. This had to be done ere electrolysis could be effected. When the electric current had entered the water, the hydrogen atom adjacent to the negative pole gave up its charge to that pole, and, having become electrically neutral, separated in the form of hydrogen gas. The oxygen atom which had been in union with this atom, combined with the hydrogen atom of the next water molecule, and thus the impulse passed along until the last oxygen atom, in contact with the positive pole, had its charge neutralized by the charge of this pole, and then escaped as oxygen gas.

The first decade of the nineteenth century also witnessed the separation of several of the alkali metals from their hydrates, by Sir Humphrey Davy; thus, potassium and sodium were first obtained by him in this manner in October, 1807.

Led thereto by the results of his experiments, Davy advanced his electrochemical theory, probably the first theory of its kind ever formulated; it rests upon the atomic hypothesis of Dalton. According to its teaching, the atoms of substances as such bear no electric charges, but they acquire positive or negative charges by contact with each other. Chemical affinity is caused by and depends on the attraction of such opposite electrical charges. Electrolytic decomposition is effected by the neutralization of these charges.

This theory of Davy's met with considerable opposition, and was soon displaced by the views advanced by Berzelius, outlined in 1812 and published in detail two years later.

Berzelius held that every atom was charged with both positive and negative electricity, and that the electrical behavior of the atom depended upon whichever of these charges was present in excess. Chemical attraction was also ascribed to electrical attraction between opposite charges; the one or the other of these predominated, and in accordance therewith the resultant compound exhibited either an electropositive or an electronegative character.

Objections to this theory of Berzelius were, however, not lacking. It was held that if the electrical charges of the atoms determined chemical union, that then the properties of a compound must be a function of those charges. The fact that three atoms of chlorine (electronegative) could be put in the place of three atoms of hydrogen (electropositive) of the methyl group in acetic acid without causing a fundamental disturbance of the nature of the compound, was an obstinate fact which Berzelius could not account for.

It remained for J. J. Thomson, in 1895, to show that an element may, according to circumstances, bear either an electropositive or an electronegative charge, and that "it would appear that the chlorine atoms, in the chlorine derivatives of methane, are charged with electricity of the same kind as the hydrogen atoms they displace."

The brilliant work and discoveries of Michael Faraday, beginning in 1832, mark the next important epoch in the history of electrochemistry.

Faraday first determined the identity of electricity produced by friction and by the voltaic pile. When he had established this, he turned his attention to the relation between the amount of electricity passing through a circuit and its magnetic and chemical effects, and found that the amount of chemical decomposition produced in an electrolyte is proportionate to the amount of electricity which passes through the electrolyte.

Faraday further studied the relation between the amounts of different elements set free from their compounds on passing a given electric current through solutions of these compounds. Among the substances which he investigated in this manner were solutions of some salts of copper, of silver, and of zinc. He thus determined that the amounts of different elements separated by the same quantity of electricity, stand in the same relation to each other as the chemical equivalents * of those elements. This means that all monovalent atoms bear the same amount of electricity, and that all multivalent atoms bear some simple multiple of this amount.

It must be especially noted that these laws of Faraday emphasize the fact that equal *quantities* of electricity separate chemically equivalent amounts of the elements; the electromotive force, the potential necessary to effect this, is not referred to at all; this factor has different values with different electrolytes, as will be discussed later.

In 1857 Clausius pointed out the shortcomings of the theory advanced by Grothuss, and suggested that solutions of an electrolyte must contain some part-molecules in addition to non-decomposed, entire molecules. This hypothesis offered an explanation of the fact that even very weak

* The chemical equivalent of an element is the atomic mass of that element divided by its valence.

currents, in some instances, can effect electrolysis, the current exercising a directing influence on the part-molecules originally present. This work of Clausius practically prepared the way for the theory of electrolytic dissociation, which was brought out thirty years later.

It was in 1887 that J. H. Van't Hoff published his valuable article on the rôle which osmotic pressure plays in solutions. This paper, in the same year, inspired the hypothesis of Planck, based on thermodynamical considerations, and the theory of electrolytic dissociation advanced by Svante Arrhenius, who was able to furnish experimental proof of the truth of Planck's assumptions, and who thus established the famous theory which to-day holds the leading place in electrochemical science. This theory will later be considered in detail.

Electrolysis. — Conductors of electricity in which substance-movement of the conducting material accompanies the passing of the electric current, have been termed conductors of the second class. In this category are included all solutions which can conduct an electric current, and also all fused salts which can act as conductors. They are all designated by the term electrolytes, and the particles into which molecules of electrolytes dissociate are termed ions.

These ions are particles of matter associated with definite charges of electricity. As Von Helmholtz, in his Faraday lecture delivered in London in 1881, expressed it: "If we accept the hypothesis that the elementary substances are composed of atoms, we cannot avoid concluding that electricity also, positive as well as negative, is divided into definite elementary portions, which behave like atoms of electricity. As long as it moves about in the electrolytic fluid, each ion remains united with its electric equivalent, or equivalents."

The terminals of the wires by which the electric current enters and leaves the electrolyte are called electrodes; the

electrode by which the current enters the electrolyte is the anode; the one by which it leaves, the cathode. The ions, charged with positive electricity, which are discharged at the cathode, are termed cathions; the negatively charged ions which are set free at the anode are called anions. The direction of current flow is understood to be the direction of the current from its point of entry into the electrolyte, at the anode, across the electrolyte, to, and emerging at, the cathode.

The distinguishing feature of electrolysis is that the products of the reaction appear only at the electrodes. It was Faraday who studied these questions of electrolytic phenomena with the utmost care, and who formulated the laws which govern these reactions. These laws have been previously referred to; they may be concisely expressed as follows:

1. The amount of a substance set free or deposited by an electric current is proportional to the quantity of electricity passing through the electrolyte.

2. The amounts of different substances separated by the same quantity of electricity bear the same relation to each other as the chemical equivalent weights of those substances.

The most rigid experimental tests to which Faraday's laws have been subjected, on the one hand by the use of very large currents of electricity (Buff, 1853), on the other hand by the use of very small electric currents (Ostwald and Nernst, 1889), as well as the most careful determinations of electrochemical equivalents, which have been made by many investigators, have, one and all, only served to demonstrate the exactness of these laws of Faraday.

The quantity of electricity which is passing through an electrolyte is conveniently ascertained by measuring either the weight or the volume of the products resulting from its electrolytic action.

Apparatus designed for this purpose are generally called voltameters, or coulometers, a name suggested by Professor

Richards, in 1902, to avoid confusing voltameters with voltmeters. Various forms of coulometers are used; the most accurate instrument of the kind is probably the silver coulometer in which metallic silver is precipitated on the cathode from a neutral solution of nitrate of silver, the anode consisting of a bar of pure silver.

Copper and mercury coulometers of analogous construction are also frequently employed. In the former, both electrodes are of metallic copper and the electrolyte is some salt of copper, generally sulphate of copper. In the mercury coulometer some mercurous salt is used as the electrolyte, mercurous nitrate, for instance. Both anode and cathode consist of metallic mercury in glass receptacles.

Another favorite form of coulometer is that in which the electrolytic decomposition of water is effected and in which the volume of the resulting gases is measured. These gases, hydrogen and oxygen, may be caught either separately or together, and their volume measured. One ampere in one minute sets free 10.45 C. C. of these mixed gases, measured at 0° C. and 760 mm. pressure. In these gas coulometers a solution of sodium hydrate or dilute sulphuric acid is generally used; if the former, the electrodes are preferably made of nickel; if sulphuric acid be employed as the electrolyte, the electrodes are both made of platinum.

As the quantity of electricity passing through any given conductor is determined by the current strength, measured in amperes, and the time during which the current flows, an identical quantity of current will flow and an identical amount of work, electrolytic or other, will result, whether, for instance, 100 amperes flow for 5 seconds, or whether 250 amperes flow for 2 seconds. It will be recalled that the amount of electricity conveyed by one ampere in one second is termed a coulomb, and that this is the quantity of electricity which will deposit 0.001118 gram of silver in a silver coulometer.

This amount, 0.001118 gram, is termed the electrochemical equivalent of silver. This term must be well distinguished from the expression chemical equivalent or equivalent weight, as it is also called. The latter, it will be remembered, is the quotient obtained on dividing the atomic weight of an element by its valency. Elements whose valency is one, the so-called monads, have their chemical equivalent identical with their atomic weight. Elements whose valency is two, dyads, have their chemical equivalent equal to one-half their atomic weight; in triads, it is one-third the atomic weight, etc. In the case of complex ions the equivalent weight is equal to the molecular weight — that is, the sum of the atomic weights of the complex ion, divided by its valency.

Application of Faraday's second law, of course, makes it a simple matter to calculate the electrochemical equivalent of every element when the electrochemical equivalent of any one element has been accurately determined experimentally.

To illustrate, let a determination of the electrochemical equivalent of zinc be required.

The atomic weight of zinc is 65.4, its valency is 2, and consequently its equivalent weight is $65.4 \div 2 = 32.7$. Accepting the atomic weight of silver as 107.93 and its valency as one, that quantity of electricity which will deposit 0.001118 gram of silver must deposit of zinc:

$$107.93 : 32.7 :: 0.001118 : x$$
$$x = 0.0003387 \text{ gram.}$$

This value is therefore the electrochemical equivalent of zinc.*

The chemical equivalent weight of a substance in grams is termed a gram equivalent of that substance. To deposit

*An excellent table of "Electrochemical Equivalents and their Derivatives," by Carl Hering, M.E., is published in *Electrochemical Industry*, New York, January, 1903.

one gram equivalent of any element requires an amount of electricity, in coulombs, equal to the chemical equivalent of that element divided by its electrochemical equivalent.

Thus, to deposit one gram equivalent of silver requires $107.93 \div .001118 = 96{,}538$ coulombs. This value varies slightly with different experimentors. The electrochemical equivalent of silver was found to be:

0.0011179 by Lord Rayleigh and Mrs. Sedgewick,
0.0011183 by W. and F. Kohlrausch,
0.0011172 by Richards, Collins, and Heimwood,
0.0011192 by Patterson and Guthe,
0.0011193 by Kahle.

Accepting the atomic weight, and hence, of course, the chemical equivalent of silver, as 107.93, and employing the several electrochemical equivalents above given, the determination by:

Lord Rayleigh and Mrs. Sedgewick	= 96,547 coulombs,
W. and F. Kohlrausch	= 96,513 coulombs,
Richards, Collins, and Heimwood	= 96,608 coulombs,
Patterson and Guthe	= 96,435 coulombs,
Kahle	= 96,426 coulombs.

We will accept the value 96,540 coulombs as the ionic charge for a monovalent gram ion, this being the value usually employed.

It can be readily shown that 96,540 coulombs are required to deposit or to liberate one gram equivalent of any element, and this quantity of electricity, viz: 96,540 coulombs is called a faraday. This constant is of the greatest importance in electrochemical work, for on passing one faraday through an electrolyte there is always set free one gram equivalent of an ion at the cathode, and one gram equivalent of an ion at the anode, provided that the electrolysis effected is simple and not complex.

If complex, that is, if more than one kind of ion is set free at one of the electrodes, the sum total of the ions thus set free at that electrode amounts to one gram equivalent. Thus, in the electrolysis of water one faraday causes the liberation of 1.008 grams of hydrogen at the cathode and of 8.000 grams of oxygen at the anode. If, however, in the electro-analysis of an alloy two metals were to be simultaneously deposited on the cathode, then the sum of the gram equivalents of these two metals so deposited would correspond to the work done by one faraday.

Taking the chemical equivalent of hydrogen as unity, one coulomb will liberate

$$107.93:1::.001118:x$$

$$x = 0.00001036 \text{ gram of hydrogen.}$$

This value, which was determined by Lord Rayleigh as 0.000010352 gram, and by Kohlrausch as 0.000010354 gram, is the electrochemical equivalent of hydrogen. The chemical equivalent of any element multiplied by the electrochemical equivalent of hydrogen is, of course, the electrochemical equivalent of that element.

Designating the chemical equivalent of any element by Z, the actual weight in grams of such element deposited by electrolysis is calculated by the formula:

$$w = 0.00001036\ Zct,$$

in which,

w = weight in grams,
Z = chemical equivalent of the element deposited,
c = current strength employed (in amperes),
t = time of passing of current (in seconds).

Or, designating the electrochemical equivalent of the element deposited by z, this formula becomes:

$$w = zct.$$

If the time be measured not in seconds but in hours T, then cT represents ampere-hours, that is to say, the quantity of electricity conveyed by the current in one hour, and the formula first given would read:

$$w = .00001036 \times 3600\, ZcT,$$
$$w = 0.037296\, ZcT,$$

or, for all practical purposes,

$$w = 0.0373\, ZcT.$$

From this formula the amount of current, C, is readily deduced which is required to set free or to deposit a given weight of an element, w, in a given time:

$$C = \frac{[1.0 \div .0373]\, w}{ZT},$$

or

$$C = \frac{26.81\, w}{ZT}.$$

The electrical power, in watts, needed to do this work is calculated by the formula:

$$EC = \frac{26.81\, wE}{ZT},$$

in which E represents the electromotive force, the voltage, employed.

At times the actual amount of chemical action obtained — take, for instance, the weight of a metal which should be deposited in an electrochemical process — does not correspond with the amount called for by Faraday's laws.

There is some diversity of opinion concerning the causes of such discrepancies. Professor Crocker* attributes the difficulty, in some instances, to the liberation of hydrogen gas in place of the metal which should be deposited; this setting free of the hydrogen may be due to an excessive current

* "School of Mines Quarterly," Vol. 22, p. 119.

density, to too great a dilution of the electrolyte, or to the great affinity which some metals have for oxygen, the consequent decomposition of the water resulting in a liberation of hydrogen. An insufficient yield of metal may also be due to a resolution of some of the metal by free acid, such acid being sometimes added in order to improve the conductivity of an electrolyte. But whatever the cause, if a discrepancy exist between the output actually obtained and the theoretical yield correctly figured according to Faraday's laws, the fault of such discrepancy will be found not to rest with the latter.

Electromotive Force. — Electrical energy has been defined as the product of two factors, quantity and intensity of electricity. Attention has been given to the former phase of the subject, now electromotive force must be considered.

Electromotive force is the pressure which drives an electric current through a conducting medium; other terms employed to designate this concept are voltage and difference of potential.

The source of the electromotive force in an electrical cell is to be sought principally at the points of contact of the electrodes with the electrolytes in which they are respectively immersed; this electromotive force is practically due to chemical action between the metallic electrodes and the chemical solutions in which these are placed.

In order that a chemical reaction may give rise to electromotive force, the substances concerned in its generation must be located apart from one another, but must be in electrical connection with each other through the agency of a metallic conductor and an electrolyte. Whenever the substances which are on one and the same side of the equation sign in a true chemical reaction are placed under the above conditions, an electrochemical process occurs.

Consider the reaction:

$$Zn + Cu\,SO_4 = Zn\,SO_4 + Cu.$$

It will be recalled that these substances form an electrolytic cell when they are arranged so that they meet the prescribed conditions; that is to say, when the zinc is away from the copper sulphate and the copper is removed from the zinc sulphate, but when both are in electrical connection by the intervention of an electrolytic medium and a metallic wire. The system here referred to is, in fact, the well-known Daniell cell.

Conversely, if under the conditions stated, electrical energy is introduced into an electrolyte, chemical changes are caused and electrochemical reactions are brought about.

To effect measurement of electromotive force, it is necessary to establish standards for comparison and to have instruments by means of which these standards may be compared with the electromotive force to be measured. An accumulator battery supplies a reliable and uniform source of current; a direct lighting current can also be used for this purpose by causing it to pass through proper resistance and by using a part of the current for the work in hand.

It is customary to employ either Clark cells or Weston Cadmium cells as standards; of these the latter are preferable, because they are scarcely affected at all by changes of temperature.

Instruments used to record voltage are either direct-reading voltmeters, or potentiometers. As it is desirable to have these instruments use as little current as possible, they are generally constructed with high resistances, this being insured by employing numerous windings of exceedingly fine wire. If a hot-wire instrument is to be used as a voltmeter, it must, of course, be put in series with high resistance.

Voltmeters are not as desirable as potentiometers because they consume some current and require occasional recalibration. To measure electromotive force with a potentiometer, the unknown force is balanced against the electromotive

force of another electric current of known value, a standard cell being used in substitution for the unknown electromotive force to be measured.*

Dissociation Voltage.— It will be recalled that one faraday, 96,540 coulombs of electricity, is the quantity of electricity which will separate one gram equivalent of any electrolyte; the amount of electrical potential required to do this, however, varies with the heat of formation of the electrolyte to be decomposed.

The amount of heat set free, or absorbed, in the formation of one gram-molecule of a substance is called the heat of formation, or, the heat of reaction of that substance. This value, in a compound, is equal to the difference between the heat of combustion of one gram-molecule of the compound and the heats of combustion of the elements which form it. It represents the loss of chemical energy of the substances which take part in the reaction.

The fact that the amount of heat necessary to decompose a compound into its constituents is precisely the same as that which was set free when this compound was formed, was determined by Lavoisier and Laplace. G. H. Hess, in 1840, formulated the law of constant heat summation: the heat given out in a chemical process is the same whether this process takes place in one or in several stages. This is practically an individual case of the law of conservation of energy, for, as energy can be neither created nor destroyed, it is evident that the amount of energy required for the decomposition of a compound must be identical with the amount of energy produced when that compound was formed.

The heats of formation of chemical compounds are given in many books on Physical Chemistry, and of course in all works dealing with Thermochemistry.†

* Confer: Lehfeldt, *liber cit.*, p. 229.

† For instance in Muir, M.M.P. and Wilson, D.M.: "The Elements of Thermal Chemistry," London, 1885.

Possessed of such thermal data, the heats of formation, there only remains to be learned the relation between the unit of heat energy and the unit of electrical energy in order to make possible a calculation of the electric potential required to effect electrolytic dissociation.

The unit of heat energy is the calorie, the amount of heat required to raise the temperature of 1 gram of water from 15° to 16° C., hydrogen scale. The unit of electrical energy is the joule — the product obtained by multiplying the coulombs and the volts of an electric current. One joule will raise the temperature of 0.238882 gram of water 1° C., hence, in round numbers, 1 joule = 0.24 calorie.

Knowing the heat of formation of an electrolyte, it is only necessary to divide this number by 0.24 to ascertain the joules required to effect the electrolytic decomposition of the compound, and the joules thus found, divided by 96,540 — or a multiple thereof — equal the number of volts required to effect the desired electrolysis.

Lord Kelvin was the first to make calculations of this kind. It is, however, important to remember that such calculations involve acceptance of the assumption that *all* of the chemical energy lost, reappears in the form of electrical energy. This, however, is by no means always the case. In some reactions, for instance, in Clark's cell (Zn : $Zn\,SO_4$: $Hg_2\,SO_4$: Hg), about 25 per cent of the chemical energy lost appears as heat. In other instances, however, the agreement between the calculated values and the values experimentally determined, is very close. Thus, for the Daniell cell (Zn : $Zn\,SO_4$: $Cu\,SO_4$: Cu), the dissociation voltage is, calculated, 1.0872 volts; experimentally determined, by Jahn at 0° C., 1.0962 volts.

To illustrate the calculation of dissociation voltage let us consider the electrolytic dissociation of potassium chloride.

The heat of formation of K Cl is 104,300 calories. The

amount of electrical energy equivalent to this amount of heat energy is, therefore,

$$104{,}300 \div 0.24 = 434{,}584 \text{ joules,}$$

and $$434{,}584 \div 96{,}540 = 4.50$$

hence, 4.50 volts is the minimum voltage required to decompose potassium chloride into its constituents, potassium and chlorine.

One faraday, 96,540 coulombs, will decompose one gram-molecular weight of an electrolyte of which both components are monovalent. Potassium chloride is such a compound;

the atomic weight of potassium	= 39.15
the atomic weight of chlorine	= 35.45
hence, the molecular weight of potassium chloride	= 74.60

Therefore, it will require 434,584 joules, or 96,540 coulombs at a potential of 4.50 volts to decompose 74.60 grams of potassium chloride into its constituents, viz: 39.15 grams of potassium and 35.45 grams of chlorine.

If the electrolyte to be decomposed has a divalent constituent, 2 faradays = $96{,}540 \times 2 = 193{,}080$ coulombs will be required to effect the desired electrolysis, and it is this number which must be divided into the joules required, to ascertain the minimum dissociation voltage. This minimum dissociation voltage may also be readily calculated by dividing the heat of formation of the compound, expressed in calories, by 23.062 times the valence, *i.e.* the number of bonds. This factor, 23,062, is obtained by dividing 96,540 ÷ 4.18617, for one calorie is equal to 4.18617 joules.

Thus, in the case of potassium chloride, where the valence is one, and the heat of formation is 104,300 calories:

$$104{,}300 \div 23{,}062 = 4.52 \text{ volts.}$$

In the case of magnesium chloride, $Mg\ Cl_2$, where there

are two bonds to be considered, we would have — taking the heat of formation of $Mg\ Cl_2$ as 217,300 calories:

$$217{,}300 \div [23{,}062 \times 2] = 4.71 \text{ volts.}$$

The dissociation voltages thus found are valid for electrolytes in aqueous solution. Fused electrolytes require somewhat lower voltages, because the heat of fusion, to a certain degree, assists the reaction.

CHAPTER IV.

ELECTROLYTIC DISSOCIATION.

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The Ion Theory. — The Theory of Electrolytic Dissociation, or the Ion Theory, as it is frequently termed, was formulated by the Swedish scientist, Svante Arrhenius, now professor in the University of Stockholm, after he had become acquainted with the brilliant researches of J. H. Van't Hoff; these were published in 1887, in an article entitled, "The Rôle of Osmotic Pressure in the Analogy between Solutions and Gases."

By the term osmotic pressure there is understood the pressure exerted by the molecules of a substance in solution when such solution is brought into contact with the pure solvent, or when such a solution is brought into contact with another solution of a different degree of concentration. All substances when dissolved in water exhibit osmotic pressure.

The true cause of osmotic pressure is as yet unknown, but the phenomena of osmotic pressure have been carefully

studied and some very important relations have been determined.

Van't Hoff's theory of osmotic pressure holds that the osmotic pressure of a substance in solution is the same as the pressure which that substance would exert if it were in the gaseous form and occupied the same volume at the same temperature. In other words, the laws of gases apply also to dilute solutions; the laws of gas-pressure are valid also for the osmotic pressure of solutions.

The gas-equation $pv = RT$ states that the product of the volume and the pressure of a gas is directly proportional to the absolute temperature and to the value R.

R is a constant $= \frac{p_0 v_0}{273}$. In the equation of state for gases:

v = volume in cc. of a gram-molecule of the gas,
p = pressure in grams per square centimeter,
T = absolute temperature.

The molecular weight in grams (1 mol) of a gas at 0° C. and 76 cm. of Hg pressure, has a volume of 22.4 liters; in the space of 1 liter it must, therefore, exercise a pressure of 22.4 atmospheres. Now it follows, according to Van't Hoff's theory, that the osmotic pressure, exercised by a solution of 1 mol of a substance in 1 liter, must likewise be equal to 22.4 atmospheres.

A solution of this kind (1 gram-molecular weight of a solute in 1 liter) is called a normal solution.

A normal solution hence exercises an osmotic pressure of 22.4 atmospheres; a tenth-normal solution exercises an osmotic pressure of 2.24 atmospheres, and so on.

It is evident, then, that if the osmotic pressure of a solution is known, that the molecular weight of the solute can be readily determined.

A 1 per cent solution of sucrose gives an osmotic pressure of 49.3 cm. of Hg.

A normal solution of sucrose would give a pressure equal to

$$22.4 \times 76 = 1702.4 \text{ cm. Hg.}$$

The 1 per cent solution contains 10 grams of sucrose per liter, hence

$$10 : x : : 49.3 : 1702.4, \qquad x = 345.$$

This is in close agreement with the molecular weight of sucrose as calculated:

$$\begin{array}{r} \text{C } 12 \times 12 = 144 \\ \text{H } 22 \times 1 = 22 \\ \text{O } 11 \times 16 = 176 \\ \hline 342 \end{array}$$

Many solutions which were examined in this way yielded returns which were found to agree with this theory and which bore out its assumptions. But it was soon ascertained that all the salts, acids, and bases did not behave in accordance with its teachings.

Solutions of these substances gave osmotic pressures *greater* than they would have given had they acted in conformity with the laws of gases.

It was furthermore determined that those substances which in aqueous solutions exert an osmotic pressure greater than is called for by the law of gas-pressure, likewise cause greater lowerings in the freezing-point of water, produce greater elevations of the boiling-point, and effect a lowering in the vapor-tension of volatile solvents: last, but not least, it was found that aqueous solutions of these substances, and these only, could conduct the electric current.

To meet the exigencies of the case it was proposed to introduce an additional factor i into the gas-equation, thus making the latter read:

$$pv = iRT.$$

This factor i was termed the Van't Hoff i, from its originator.

In all of the substances named, the salts, the acids, and the bases, the value of i is always greater than unity.

Arrhenius, reflecting on this problem, on the probable cause of these numerous discrepancies between Van't Hoff's theory of osmotic pressure and the results found, recalled the analogous case of abnormal vapor-pressures exhibited by iodine and by some other substances when their vapor-pressures were determined at high temperatures.

In these instances the explanation had at last been reluctantly accepted, that a dissociation of the molecules probably occurred at high temperatures.

"Therefore," wrote Arrhenius, "it is natural to assume that substances which in aqueous solution give pressures that are too great, are likewise dissociated."

Arrhenius outlined his theory in a letter which he addressed in the early part of 1887 to Oliver Lodge, secretary of the British Association Committee for Electrolysis. Somewhat later in the same year a full discussion of his views appeared in the *Transactions of the Swedish Academy of Sciences*, in which journal there had been published, in 1883, another article by Arrhenius, "Galvanic Conductivity of Very Dilute Aqueous Solutions," in which he may be said to have, in a measure, foreshadowed the theory of electrolytic dissociation which he formulated in 1887.

The essence of this theory of Arrhenius is, of course, the deduction that the osmotic pressure exercised by the particles into which molecules may become dissociated is the same as the osmotic pressure exercised by the molecules themselves.

In other words, the ion theory holds, that in dilute aqueous solutions there are more smallest particles of the dissolved substance (the solute) than correspond to the molecular weight of the substance; the theory accounts for this by assuming that a number of molecules are dissociated, electrolytically dissociated, in such solution.

On the assumption that the forces holding chemical atoms together in molecules are of electrical origin, J. J. Thomson explains electrolytic dissociation of molecules into ions by means of electrical induction.

On introducing an electrolyte, sodium chloride, for instance, into a dissociant solvent, say water, the positive atom, the sodium, will induce a negative charge in the water, and the negative atom, the chlorine, will induce a positive charge in the water. These induced electric charges almost neutralize the electric charges on the atoms which originally induced them, and thus the attraction between the atoms of the original molecules is weakened and dissociation ensues.

The amount of energy possessed by two electric charges held apart by any medium is inversely proportional to the specific inductive capacity — the so-called dielectric constant of that medium.

The dielectric constant of water is 80. Calvert ascribes a dielectric constant of 92.8 to hydrogen peroxide; that of hydrocyanic acid is 95. In consequence of the high specific inductive capacity of water electrolytic dissociation ensues readily in this medium.

The actual existence of free ions in electrolytes, the fact that they bear charges of electricity, and that they migrate under the influence of electric force, was experimentally demonstrated by Ostwald and Nernst. It is the movement of these electric charges which constitutes an electric current within an electrolyte.

As previously stated, when an electric current passes through a conducting solution, part of the ions formed in the solution move towards the negative electrode, the cathode. These particles are termed cathions; they bear charges of positive electricity. The other ions move towards the positive electrode, the anode; these ions are termed anions and they bear charges of negative electricity.

These terms are derived from the Greek: Ion means wan-

derer; cathion means descending, because the cathions in the electrolyte move with the positive current towards the cathode; anion means ascending, to indicate that the anions move in a direction opposite to that taken by the cathions. This terminology is due to Faraday.

Williamson, in 1851, and again Clausius, in 1857, assumed that a small portion of ions preëxisted in solutions and that these were capable of conducting the electric current; these particles were designated as part-molecules.

In 1887, however, it was generally believed that the electric current itself induced the breaking up of chemical compounds into the particles which conveyed the electric charge through solutions capable of conducting electricity.

It was Arrhenius who determined that the number of preëxistent ions might be considerable, and that, up to a certain limit, dilution of the solution increased their number.

An equivalent amount of positive and of negative electricity must always be conveyed by the ions, for no free electricity can be detected in solutions of electrolytes, hence for every cathion which separates at the cathode, an anion must give up a corresponding electric charge at the anode.

Ions possess definite electric valencies, and for every dyad ion which separates at one electrode, another dyad ion or two monovalent ions must separate at the other electrode. Among the more important monovalent cathions are:

H (in the acids), K, Na, Ag. . . .

Among the divalent cathions:

Ca, Ba, Mg, Fe (in ferro-compounds), . . .

Among the trivalent cathions:

Al, Bi, Sb, Fe (in ferri-compounds), . . .

Among the monovalent anions:

OH (in the bases), Cl, Br, I, NO_3, ClO_3 . . .

Among the divalent anions:

$$S, \quad SO_4, \quad MnO_4 \ldots\ldots$$

The following table of the chemical elements in their electrochemical sequence, is given by N. Monroe Hopkins. Each element is electropositive to every element whose name is placed before its own, and is electronegative to all elements whose names follow its own:

Negative Atoms.

Oxygen	Fluorine	Bromine
Sulphur	Chlorine	Iodine
Nitrogen		

Positive Atoms.

Selenium	Platinum	Lanthanum
Phosphorus	Rhodium	Didymium
Arsenic	Ruthenium	Cerium
Chromium	Palladium	Thorium
Vanadium	Mercury	Zirconium
Molybdenum	Silver	Aluminium
Tungsten	Copper	Scandium
Boron	Uranium	Erbium
Carbon	Bismuth	Ytterbium
Antimony	Gallium	Beryllium
Tellurium	Indium	Magnesium
Tantalum	Germanium	Calcium
Columbium	Lead	Strontium
Titanium	Cadmium	Barium
Silicon	Thallium	Lithium
Tin	Cobalt	Sodium
Hydrogen	Nickel	Potassium
Gold	Iron	Rubidium
Osmium	Zinc	Cæsium
Iridium	Manganese	

It must, however, not be forgotten that the terms positive and negative in electricity are merely relative — it all depends on the conditions in which the substances are placed.

If two metals are placed in a solution which attacks the one metal and does not attack the other, the metal which goes into solution is electropositive to the other metal; the metal which goes into solution forms the negative pole in the outside circuit.

Zinc is attacked by dilute nitric acid and by dilute sulphuric acid, and even in solutions of ammonium chloride and potassium hydrate it will go into solution replacing other metals; zinc, therefore, is electropositive to them all.

It has been previously explained that all ions of the same valency bear identical electric charges, although the masses of the atoms with which these charges are associated are not equal. Ions, in short, may be regarded as combinations of material atoms with electric atoms, with the so-called electrons.

Ions of different substances vary considerably in their electro-affinity, that is, in the degree of power with which they hold their electric charges. Those ions which hold their electric charges firmly are termed strong, those which readily part with their charges are called weak ions. As a rule, strong ions are given to the forming of soluble compounds, compounds which dissociate readily when brought into solution. Weak ions, on the other hand, are generally given to the forming of compounds which are less soluble, that is, to the forming of compounds which ionize only to a slight degree when placed into contact with a solvent.

If an ion of a low degree of electro-affinity encounters a non-ionized substance which possessess a greater degree of electro-affinity when in the ionic state than it itself possesses, then the electric charge will be transferred from the former to the latter.

For instance, if metallic zinc is brought into contact with lead in the ionic condition the lead suffers precipitation as metallic lead, while the zinc goes into solution, zinc ions being formed. Lead precipitates copper; copper, in turn, precipitates mercury, and so on.

When an electric current is passed through an electrolyte the ions move through the solution to the electrodes and there give up their charges of electricity, provided that the tension of the electrodes is sufficient to overcome the electro-affinity of the ions for their electric charges. When this happens the atoms separate in their elemental condition, unless they take part in some secondary reactions in which they enter into new chemical relations.

The capacity of forming ions does not depend alone on the substance which goes into solution, the solvent plays an important rôle in this transaction. This property is referred to as the dissociative power of the solvent. Water, as previously mentioned, has a high dissociant power; formic acid, methyl and ethyl alcohol are fairly strong dissociants. Chloroform, benzol, and many other organic substances lack this dissociant power entirely; these substances are, therefore, not electrolytes, that is, they do not conduct an electric current between electrodes immersed in them.

Gram-molecular equivalent solutions of most neutral salts are practically completely ionized in 1000 liters of water. As a rule, salts containing monovalent ions are ionized to a greater extent than salts of multivalent ions.

The strong acids, among which must be counted hydrochloric, hydroiodic, hydrobromic, nitric, and sulphuric acids, are under like conditions all ionized to about the same degree as the salts. Phosphoric and sulphurous acids are usually ionized to the extent of only 10 per cent; silicic acid and boracic acid are hardly ionized at all.

Walker and Cormack have determined the degree of ionization of the following substances in one-tenth normal solutions:

Hydrochloric acid	91.4%
Acetic acid	1.3%
Carbonic acid	0.174%
Sulphuretted hydrogen	0.075%
Boracic acid	0.013%

Among the strong bases are the hydroxides of the alkalies and the hydroxides of the alkaline earthy metals. Ammonia and magnesia are bases of a lower degree of ionization, and the hydroxides of the di- and tri-valent metals and most of the alkaloids must be counted among the weak bases.

The ion theory has proven of special value in the securing of a clearer understanding of the problems of analytical chemistry, and it is to Wilhelm Ostwald that science is chiefly indebted for signal achievements in this direction.

The study of many, if not of most chemical reactions, may be regarded as a study of the behavior of ions, for ions have and preserve certain individual characteristic properties, which they exhibit without regard to the presence or absence of other ions and molecules. The properties of aqueous solutions of most salts are but the sum of the properties of their constituent ions.

That this point of view materially simplifies analytical chemistry is evident when one considers that instead of having to study and to remember the reactions of, say, one hundred different compound substances, all that it is necessary to know are the reactions of ten cathions and ten anions which enter into the composition of the above-named one hundred compounds.

The terms salt, acid, and base, have here been repeatedly used, and it will be necessary to give their definitions as understood in the light of the ion theory. Salts are compounds which, when they are dissolved, break up, wholly or in part, into cathions and anions. Acids are salts in which the cathions are always hydrogen ions; bases are salts in which the anions are always hydroxyl ions.

Strong acids are those which contain numerous hydrogen cathions in unit volume — for the characteristic properties of acids depend on their hydrogen ions.

Strong bases are those which contain many hydroxyl anions in unit volume, for it is upon the presence of the

hydroxyl ions that the characteristic properties of bases depend.

Acidity and basicity of solutions hence rest solely upon, and vary with, respectively, the amount of hydrogen and of hydroxyl ions present.

The hydrogen ions of acids behave differently from hydrogen occurring in other combinations; the hydroxyl ions of bases likewise react differently from the hydroxyl groups occurring in other compounds. Thus, the hydrogen ions of acids will redden litmus; the hydroxyl ions of bases will turn red litmus blue. Water and hydrogen peroxide both contain hydrogen and hydroxyl, yet neither shows the above-mentioned reactions with litmus. Water and hydrogen peroxide are, therefore, at once recognized as not belonging to either the acids or bases.

Pure water is ionized only to a very slight degree, less than one mol, that is to say, less than 18 grams in 10,000,000 liters — 14 grams is the figure that approximates more closely to the real value. To express it differently, in one million liters of water there are 0.078 grams of hydrogen ions and 1.326 grams of hydroxyl ions. These values are the values for the temperature of 18° C. The number of ions in a given solution increases very rapidly with the temperature, approximately at the rate of 8 per cent per degree. As water is so slightly dissociated, it is but natural that hydrogen ions and hydroxyl ions when they meet in a solution should immediately combine to form non-dissociated water.

From the viewpoint of the ion theory the neutralization of an acid in an aqueous solution is looked upon, not as the union of an acid with a base radical, but as the union of the hydrogen ions of the acid with the hydroxyl ions of the base; the process of neutralization in an aqueous solution hence consists essentially in the formation of water.

The heat of neutralization, for instance, of the reaction:

$$HCl + NaOH = Na + Cl + H_2O,$$

is due to the heat of chemical combination of the hydrogen ions with the hydroxyl ions, the sodium cathions and the chlorine anions remaining unchanged in the solution.

Bearing in mind that an ion consists of the atom of an element plus one, two, three, or more electric charges according to its valence — a fraction of the unit charge is never carried — ions can, in writing, be readily differentiated from the atoms of elements by adding to the chemical symbols for the latter some conventional sign to indicate the character of the electric charge the ions bear, and to specify the number of these charges.

A small circle or period has been selected to represent a charge of positive electricity, a dash or a comma, to typify a negative charge; the number of these symbols indicate the number of electric charges borne by an ion. Thus, an ion of hydrogen is represented by the symbol $H^{\bullet}$, an ion of calcium by the symbol $Ca^{\bullet\bullet}$. The anion chlorine, is Cl'; oxygen O''; the complex anion hydroxyl, OH'.

The term ion, introduced by Faraday, was by him employed in connection with the stems of the chemical names of substances to indicate the substances from which the ions originated. A systematic nomenclature of the ions has, however, as yet, not been adopted, although James Walker * has proposed a system of naming, as he expressed it, "the material of the ions as distinguished from the particles themselves." Cathions he would indicate by adding the termination *ion* to the stem of the word, and, when necessary, would disclose the electrical valency of the ion by prefixing a Greek numeral. Thus he suggested:

Hydrion	$H^{\bullet}$
Sodion	$Na^{\bullet}$
Calcion	$Ca^{\bullet\bullet}$
Diferrion	$Fe^{\bullet\bullet}$
Triferrion	$Fe^{\bullet\bullet\bullet}$

* *Chemical News*, 1901, Vol. 84, p. 162.

The names of the anions he proposed forming in such a manner as to indicate the kind of salt from which the anions are derived. For instance, anions formed from *-ate* salts would have the termination *-anion;* those formed from *-ite* salts, the ending *-osion* — to recall the *-ous* acids which give rise to *-ite* salts. Anions from *-ide* salts would receive the termination *-idion.* For instance:

Hydroxidion	OH'
Sulphidion	S''
Sulphosion	SO_3''
Sulphanion	SO_4''

The term ionogen has been suggested by Alexander Smith * to indicate any and all substances which can suffer ionization.

When a solid goes into solution it exercises pressure, the so-called solution-pressure, and this corresponds to the osmotic pressure of a saturated solution. If the molecules of a solid are not dissociated in the process, the action ceases when a certain pressure has been attained; if the substance is an ionogen, the action continues until the ions and the non-dissociated molecules respectively have attained to a definite concentration.

This relation can be expressed by a formula which holds true in many, but not in all, instances:

$$Km = ca.$$

In this formula:

K = the constant of ionization,
m = the concentration of the non-dissociated molecules,
c = the concentration of the cathion,
a = the concentration of the anion.

The unit of concentration is one mol per liter. In other words, the formula $Km = ca$, where it is valid, states that

* *Chemical News,* 1901, Vol. 84, p. 279.

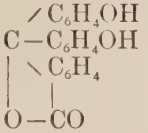
the product of the ions present in a solution bears a fixed relation to the amount of non-dissociated molecules in that solution.

This formula is an interesting one. Nernst determined that the concentration of the non-dissociated molecules does not change in a saturated solution; in a case where both m and K are unchanging the product ca must also have a constant value. This product is termed the solubility product. It represents the number of grams per liter to which the concentration-product of the ions can attain and yet have the ions exist as ions in the solution.

Should one add to a saturated solution wherein such an equilibrium obtains, any other solution which has an ion in common with an ion of the solution first named, then the equilibrium would be disturbed and the solubility-product having been exceeded, the respective values would suffer readjustment. This indicates the condition which must be established in order to secure a practically complete precipitation of any given substance, an excess of the precipitating reagent must be employed. The same principle applies to the washing of precipitates; in order to avoid the solvent action of the washing-fluid care must be taken to have the washing-fluid contain ions identical with some of those instrumental in forming the precipitate.

The ions of most of the lighter-weight metals, and those of the halogens, are colorless; those of the heavier metals are colored; for instance, cobalt ions are red, nickel ions and di-ferric ions are green. The use of indicators in acidimetry and alkalimetry is based on the fact that in the indicators used the color of the non-dissociated molecule is different from the color of the ion or ions formed therefrom. The ion theory affords a plausible explanation of the phenomena involved and it will be of interest to consider a case in illustration; phenolphthalein, which is much used as an indicator, will answer the purpose.

The formula of phenolphthalein is $C_{20}H_{14}O_4$. Its configuration is probably



Phenolphthalein is a weak acid, that is to say, it ionizes in water only to a slight degree. Its non-dissociated molecule is colorless, its cathion $H^{\bullet}$ is colorless, its complex anion is red. This anion shall here be denoted by the symbol $P.P'$.

If KOH is added to a colorless (alcoholic) solution of phenolphthalein there will be present in the solution:

Ions from phenolphthalein: $H^{\bullet}$ cathions and $P.P'$. anions;

From the KOH solution: $K^{\bullet}$ cathions and $(OH)'$ anions.

The $H^{\bullet}$ cathions of the phenolphthalein will combine with the $(OH)'$ anions of the potassium hydrate and form non-dissociated water-molecules. Abstraction of the $H^{\bullet}$ cathions will, however, induce other molecules of phenolphthalein to dissociate in order to restore the equilibrium indicated by the formula $Km = ca.$

These reactions continuing, there will ultimately be present in the solution an accumulation of $K^{\bullet}$ cathions and of complex phenolphthalein anions. The latter, as previously stated, are red and hence — so says the ion theory — the red color of the solution.

By means of the reactions indicated, the potassium-salt of phenolphthalein has been formed. As a rule the potassium salts of weak acids are ionized to a greater degree than the acids from which they are formed. In consequence, the solution contains toward the end of the reaction a greater number of phenolphthalein anions, and these impart the red color to the solution.

If a strong acid, hydrochloric acid, for instance, be added to a solution of this description, then there would be present in the solution:

Ions from the potassium-salt of phenolphthalein: $K^{\cdot}$ cathions and P. $P.'$ anions.

Ions from the hydrochloric acid: $H^{\cdot}$ cathions and Cl' anions.

The $H^{\cdot}$ cathions would come into contact with the phenolphthalein anions, and as the ionization constant of phenolphthalein, a weak acid, is smaller than that of its potassium salt, the $H^{\cdot}$ cathions and the phenolphthalein anions would recombine to form non-dissociated phenolphthalein. These molecules are colorless and in consequence the solution would lose its red color which, it will be remembered, was caused by the phenolphthalein anions. The solution would again turn colorless.

Litmus is an acid indicator; azolithmin is its active coloring principle. The non-dissociated molecules are red, the anions are blue. Addition of a base to litmus results in the formation of water and of a more highly ionized salt, and the blue color of the anions imparts a blue color to the solution. Addition of a strong acid to such a solution will cause some of the original non-dissociated red molecules of litmus to reform, and, in consequence, a red color will again appear.

If titrations are attempted in very dilute aqueous solutions, then the $H^{\cdot}$ cathions and the $(OH)'$ anions of the water will take an active part in the reaction. This phenomenon is referred to as hydrolytic dissociation, or hydrolysis.

Hydrolysis is apt to prove a serious cause of disturbance when weak acids or weak bases are titrated. In the case of strong acids and strong bases, that is to say, with those that are ionized to a considerable extent, hydrolysis is a matter of but little moment.

An example of hydrolytic dissociation is afforded by the sodium salt of phenol. On ionization this yields $Na^{\cdot}$ cathions and phenol C_6H_5O' anions. The latter enter into chemical union with the $H^{\cdot}$ cathions of the water used as solvent and, as a result, phenol, C_6H_5OH, is formed. This can be

distinctly recognized by its odor. The $(OH)'$ anions formed by the ionization of the water impart an alkaline reaction to the solution.

An aqueous solution of cyanide of potassium affords another illustration of hydrolytic action. In consequence of such action the solution always contains an appreciable quantity of HCy. The reaction of the solution is alkaline; this is owing to the presence of hydroxyl anions.

Application of the principles of the ion theory to problems of physiological chemistry has also led to some very interesting results, but a consideration of these here would take us too far afield.

The principal lines of evidence to be adduced in support of the theory of electrolytic dissociation, are in brief resumé, the following:

a. The parallelism of behavior of electrolytes and gases — osmotic pressure phenomena.

b. The abnormal lowering of the freezing-point of solutions by electrolytes. Where all normal solutions of non-electrolytes, *i.e.*, solutions containing one gram-molecule of solute in one liter of solvent, lower the freezing-point of pure water 1.86° C., all electrolytes depress the freezing-point of pure water to a much greater degree, possibly again as much.

c. The abnormal elevation of the boiling-point of water by electrolytes. Normal solutions of non-electrolytes raise the boiling-point of water by a given amount, identical for all non-electrolytes; electrolytes in normal solutions effect this to a much higher degree.

d. The thermal-neutralization phenomena of acids and bases. The neutralization of a normal solution of an acid by a base, or *vice versa*, liberates an amount of heat that is constant, 13,700 calories. This value represents the heat of formation of water, and only this. In all neutralization experiments of the kind referred to, water is an invariable

product. If molecules were formed of the other constituents, besides the molecules of water produced by the chemical combination of the hydrogen and hydroxyl, their respective heats of formation would be manifest in the reaction. This, however, does not occur, and hence the inference is drawn that these constituents exist in the solution as ions, and not as molecules.

To cite an illustration:

$$NaOH + HCl = NaCl + H_2O$$

The heat of this reaction is 13,700 calories, the molecular heat of formation of water.

The heat of formation of NaCl is 9760 calories, and yet this heat value does not appear. Why not? The reason is, because the compound NaCl is not formed in the reaction, the components of this compound remaining in the solution as ions, as ions of sodium and of chlorine.

e. The fact that chemical reactions will not take place between perfectly dry electrolytes; a dissociant is required to loosen the affinity between the atoms of the molecules and thus set free the ions which are assumed to be the reacting units of all chemical changes.

A great many data may be offered in support of the theory of electrolytic dissociation. However, it must not be overlooked that a number of facts, experimentally obtained, have as yet not been brought into harmony with its teachings.

Louis Kahlenberg* cites among other objections to this theory, that the color of solutions is independent of their ability to conduct electric currents, whereas the ion theory holds that the color of aqueous solutions, at least, is due to their ions; he denies that free ions are the immediate

* *Journal Phys. Chem.*, 1901, Vol. 5, p. 339; *Trans. Faraday Soc.*, 1905, Vol. 1, p. 42.

agents concerned in chemical reactions, for the reason that such reactions occur also in solutions that are insulators, for instance, in benzene.

Again, the theory does not, as yet, accord sufficient weight to the part which solvents play in the formation of solutions. The interesting relations which rest on the interdependence of solute and solvent still call for much further research and explanation. Furthermore, numerous thermochemical data appear to be at variance with the values the theory would seem to call for; its teachings are not always valid even for fairly dilute solutions. Reychler actually asserts the theory of electrolytic dissociation to be in opposition to many thermochemical data secured by experiment.

Notwithstanding these shortcomings, there can at least be no doubt or question as to the great value of the ion theory in the harmonization and correlation of numerous data, and of the stimulus which it has given to scientific thought and inquiry. Considering its bearing on the electron theory, it is an interesting fact that the electric charges transported by ions in electrolytes are identical with the charges conveyed by the particles in gases when electric discharges are passed through gases.

Conductivity. — By conductivity in general, there is meant the property of conducting a current of electricity. In an electrolyte, it is the joint effect of convection of the cathions and anions; it is an additive property; and the conductivity of an electrolyte represents the amount of electricity which is conveyed in unit time by unit electromotive force.

Conductivity is the reciprocal of resistance; the greater the latter, the smaller the conductivity. Conductivity is usually expressed in terms of a unit styled the mho cubic-centimeter unit; the term mho is simply the word ohm reversed in order to indicate that the unit of conductivity is the reciprocal of the unit of resistance. This unit ohm

expresses the conductivity of a substance one centimeter-cube of which has a conductance of one mho between two parallel sides. In other words, if a current density is stated in amperes per square centimeter and the potential gradient in volts per centimeter, the conductivity will be expressed in mhos per centimeter cube.

It has been experimentally demonstrated that the transmission of electric impulses through electrolytes is practically instantaneous. This can only be accounted for by the assumption of the presence of free ions about the electrodes which give up their charges the instant an electric current is sent through the electrolyte.

From the interesting researches of N. Monroe Hopkins* it appears that "electrolytes of equal resistance conduct the electric current with a definite velocity, regardless of the composition of the electrolytes or the length of the containing vessel." This investigator also determined, that an electrolyte conducts the electric current just as fast as a metallic conductor, provided, that an equal ohmic resistance, of a non-inductive type, is furnished.

Molecular conductivity is the appellation given to the conductivity of solutions which contain one gram-molecule of the electrolyte; it increases with the temperature and with the degree of dilution. As first pointed out by Kohlrausch the molecular conductivity of an electrolyte is equal to the sum of the velocities of migration of the ions.

Let, m = molecular conductivity,
a = velocity of migration of the anion,
c = velocity of migration of the cathion,
x = fraction of electrolyte dissociated into ions,
then, $m = x\,(a + c)$.

On attaining to infinite dilution the dissociation of an electrolyte into its ions becomes complete, and in that case,

$$x = 1, \quad \text{and} \quad m\infty = a + c.$$

* *Scient. Am. Suppl* 1905, p. 24305.

From these equations it follows that,

$$x = \frac{m}{m_\infty}$$

which expresses the fact that the degree of dissociation at any dilution is equal to the ratio of the molecular conductivity at that state to the molecular conductivity at infinite dilution.

Equivalent conductivity is the conductivity of equivalent quantities; it is the quotient obtained by dividing the concentration into the conductivity.

Let K = conductivity,
η = concentration in gram-equivalents per cubic centimeter,
v = volume in cubic centimeters per gram-equivalent, i.e., the dilution,
Λ = equivalent conductivity,

then, $$\Lambda = \frac{K}{\eta},$$

or, $$\Lambda = Kv.$$

The equivalent conductivity of an electrolyte, base or acid, increases with dilution, but for infinitely great dilution approaches a finite limit. Direct measurement of the equivalent conductivity of an electrolyte can be made by placing a one gram-equivalent solution between two electrodes set one centimeter apart, these electrodes serving as two walls of the vessel containing the electrolyte.

The direct determination of conductivity of an electrolyte by passing an electric current through an electrolyte of uniform cross-section and measuring the current strength and the voltage direct between the electrodes, is not always feasible, as in many instances the electrodes become polarized. In such cases the measurement is effected by aid of

an alternating current which precludes the polarization of the electrodes, each of the electrodes serving alternately as anode and as cathode.

The method of Kohlrausch, a modified Wheatstone bridge arrangement, is frequently used in determining the resistance of an electrolyte. An alternating current from the secondary of a small induction coil is employed for the reason given, and a telephone receiver is used in place of a galvanometer. When the Wheatstone bridge is not in balance a humming noise is heard in the telephone; in making the measurement the bridge resistance must be adjusted in such a way as to secure silence, or, at least, a minimum of sound. Electrodynamometers may also be used in place of the telephone arrangement. As the conductivity of an electrolyte is greatly affected by changes in temperature, the vessel in which the measurements are made should be placed in a thermostat.

Pure solids at ordinary temperatures have but a low conductivity. It is therefore of interest to know that some substances, notably the salts, exhibit a high conductivity when fused; this conductivity increases with a rising temperature.

The specific conductivity of fused nitrate of silver at 310° C. is, for instance, expressed in reciprocal ohms, equal to 1.09; at 375° C. it is 1.32. The specific conductivity of nitrate of silver in solution, dissociated into ions to the extent of about 75 per cent, is only 0.11 reciprocal ohms at a temperature of 25° C.; the conductivity of the fused salt therefore far exceeds that of the salt in solution.

Thus far it has been found impossible to determine the degree of dissociation of a fused salt into ions, and their conductivity values can therefore only be determined at given temperatures. R. Lorenz* has, however, demonstrated that the laws of Faraday are valid also for fused salts.

* *Zeitschr. für Elektrochemie*, 1900, p. 277 ; 1901, p. 753.

The fact that certain metallic oxides when at very high temperatures, though not in a state of fusion, will conduct electricity has been taken advantage of by Nernst in the making of his incandescent lamps, the filaments of which consist of oxide of magnesium; the same property has also been made use of in the construction of the tantalum lamps manufactured by Siemens & Halske.

Migration of Ions. — An electric field is a space wherein electrical influences are exerted. An ion moving in a field which is uniform is acted on by a constant force, but the speed with which it moves is not a uniformly accelerated speed, as might be supposed, because the resistance of the liquid through which the ion moves causes its velocity to be materially retarded. The intensity of the electric field in which an ion moves determines its velocity; this is called the potential gradient, and is expressed in volts per centimeter.

The velocity of an ion under a gradient of one volt per centimeter is termed its mobility, and this is, as shown by Bredig and Ostwald, a periodic function of the atomic weight of the elements. Hence the mobilities of the different ions differ, and the determination of these values is a matter of importance.

The relative mobility of anions and cathions was determined by Hittorf in the following manner: Two porous plates were inserted in a trough dividing the trough into three compartments. These compartments were all filled with an electrolyte, for instance, with a solution of sulphate of copper; a copper anode and a copper cathode, respectively, were inserted in the end compartments, and an electric current was passed through the solution.

After the current had been passed through the electrolyte for a short time, samples were taken from each of the three compartments and analyzed. The sample removed from the cathode chamber was found to be less concentrated, the

sample from the anode chamber was found to be more concentrated than before the current was passed, while the sample from the middle chamber was found to have retained its original concentration.

Taking the whole current conveyed as unity, and x as that part of the current conveyed by the anion, then $1 - x$ of course represents the fraction of the current transported by the cathion. One faraday requires one gram-equivalent of ions for its transport, in consequence there must pass across any section in the interior of the liquid x equivalents of anions in the direction opposite to the direction taken by the current, and $1 - x$ equivalents of cathions in the direction of the current. This x is known as Hittorf's number, the migration ratio of the anion.

Electric currents produced by the movement of the ions are proportional to their mobilities:

$$\begin{matrix}\text{cathionic} \\ \text{current}\end{matrix} : \begin{matrix}\text{anionic} \\ \text{current}\end{matrix} :: 1-x : x$$

The loss in concentration of the solution in the cathode compartment is equal to the gain in concentration of the solution in the anode compartment. If, for instance, in the case just discussed, 0.2 faraday had passed and the change, in each chamber, had been found to be 0.124 equivalents, the migration ratio of the anion would be:

$$0.124 \div 0.2 = 0.620$$

Values differing slightly from this have been found by different experimenters, but the true value undoubtedly closely approximates to the figure given.

Hittorf, the pioneer in this line of work, carried out a great number of determinations on migration ratios; the form of apparatus for the study of individual cases being, of course, suitably modified to meet the requirements of the occasion. A convenient model for the demonstration

of Hittorf's theory of the migration velocities of ions, has been described by Getman.*

Several methods have been devised for measuring the absolute velocities of ions, among others by Whetham and Lodge. The latter measured the absolute velocity of hydrogen ions in the following manner. Into a hot aqueous solution of gelatine, which he prepared, he incorporated some sodium chloride as an electrolyte and colored the whole mass red by the addition of a little alkaline solution of phenolphthalein. This gelatine preparation, while hot, he poured into a straight glass tube, both ends of which were bent at right angles. Each end of the glass tube dipped into a beaker containing dilute sulphuric acid; in one of these beakers a platinum anode was placed, in the other, a platinum cathode, and a voltmeter was joined across these electrodes to indicate the potential gradient of the current.

As soon as an electric current was sent through the system, hydrogen ions proceeded to pass from the anode through the gelatine preparation in the glass tube to the cathode in the other beaker. The hydrogen ions displaced the sodium from the sodium chloride, and, combining with the chlorine, formed hydrochloric acid. This acid, of course, at once decolorized the phenolphthalein, and thus the progress of the reaction could be closely traced and accurately measured.

Through careful experiments of this kind Lodge ascertained the velocity of a hydrogen ion to be 1.1580 centimeters per minute, or less than three-quarters of a meter per hour, a low speed at best, and yet the hydrogen ions exceed all others in speed of migration.

The absolute velocity of some one ion having been accurately determined, the absolute velocities of other ions can be easily deduced from their relative velocities, values which, it will be remembered, can be readily determined by Hittorf's method.

* *Science*, 1905, Vol. 21, p. 153.

CHAPTER V.

ELECTRO-ANALYSIS.

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Electro-Analysis. — Various conceptions have been and are entertained of the nature of the electrolytic process, but in view of the most recent developments it may, perhaps, be best to look upon the phenomena occurring in the electrolysis of solutions as actions and reactions in which ions play the leading rôle.

It will be recalled that ions are defined as compounds of atoms and electrons. Under the influence of the electric current the ions move towards the electrodes, of course the anions seeking the anode and the cathions seeking the cathode. When the ions have come within acting distance of the electrode towards which they are traveling, a discharge, that is to say, a neutralization of the electric charges which they bear, takes place. This division of ions into electrons and into atoms, which were held in combination with these electrons, liberates the atoms in a condition in which their chemical affinity can come most strongly into play. This condition is frequently designated as the nascent state, the

"status nascendi"; if the ions which have thus suffered discharge are compound ions, the materialistic nuclei which remain are unsaturated compounds, and as such also display strong chemical affinity.

If there is no other substance present in an electrolytic solution with which the atoms or unsaturated nuclei can enter into chemical combination, these atoms or nuclei assume the molecular state. Thus, for instance, in the electrolytic decomposition of water, if the hydrogen and oxygen set free find no other substance present with which they can enter into chemical combination, then these elements are liberated as hydrogen and as oxygen gas respectively.

The electric discharge of ions takes place in accordance with Faraday's laws. If the conditions are such that several reactions may occur, the speed with which ions are discharged is a very important factor, for, if the speed of reaction of the discharged ions with the depolarizer is greater than the speed of discharge of the ions then there will be no liberation of the discharged ions in the molecular state; this can frequently be observed in processes of oxidation and reduction.

As electrochemical reactions are confined to the immediate neighborhood of the electrodes, the rate at which such reactions proceed is dependent upon the concentration of the ions. But the concentration of the ions is determined by the current strength, the size of the electrode surface, and the concentration of the depolarizer, and these items must therefore be very carefully considered and adjusted in every electrolytic operation to ensure the desired result.

The chief characteristic of an electrolytic process, as compared with a purely chemical process, is the consumption of energy in the former in lieu of the consumption of material in the latter; in other words, an electric current effects changes, for instance, oxidations and reductions, which in chemical

processes are induced only by the intervention of chemicals. If a chemical change is brought about directly by the action of electrical energy, if the electric current is allowed to act upon an electrolyte, the action is spoken of as a direct action; if the electric energy must first suffer transformation into some other form of energy, for instance, into heat or light, the process is spoken of as an indirect action. The manner in which the electric action known as the silent discharge is effected is as yet but little understood, although unquestionably many electrochemical effects in nature are brought about by this agency.

In effecting the electrolysis of organic substances two cases must be distinguished: the body acted upon may be an electrolyte, or it may be a non-electrolyte.

In the latter case the ions which are to transport the electric charges must be furnished from some other source, through addition of some electrolyte. The ions thus introduced will, under the influence of the electric current, travel towards the electrodes, and the organic substance is acted upon by these ions only at the moment of their discharge. A substance thus entering into chemical combination with the atomic constituent of an ion at the moment of its discharge is termed a depolarizer.

Two classes of depolarizers may be distinguished, anodic and cathodic depolarizers.

Cathodic Depolarizers. — The process taking place at the cathode is termed reduction; the principal cathions, that is, the ions liberated at the cathode, are ions of the metals and of hydrogen; a few organic cathions are also known. Substances which can either take up hydrogen or give out oxygen, or do both, are known as reducible substances; in other words, they are oxidizing agents, and their special function is the neutralization of positive charges.

Anodic Depolarizers. — Anodic depolarizers are agents which destroy negative charges. If oxygen be added, or

if hydrogen be abstracted, or if both of these phenomena proceed simultaneously, the process is designated as a process of oxidation.

Thus, a substance submitted to:

REDUCTION,	OXIDATION,
Gains hydrogen,	Loses hydrogen,
Loses oxygen, or both.	Gains oxygen, or both.

Reversible Reactions and Cells. — A process at a given electrode is reversible when the substances formed in this process are the same, whether the electric current flows from this electrode or towards it.

Thus, in the Daniell cell:

$$\text{Zn} : \underset{\text{solution}}{\text{ZnSO}_4} : \underset{\text{solution}}{\text{CuSO}_4} : \text{Cu}$$

if the electric current flows from the zinc into the electrolyte zinc ions will go into solution; if the current is sent in the reverse direction, zinc ions will travel towards the zinc electrode and zinc will be deposited on that electrode.

Electrodes reversible with respect to cathions are termed electrodes of the first order; these generally consist of a metal placed in a solution of some one of its own salts. Electrodes reversible with respect to anions are termed electrodes of the second order; these can be made by placing some insoluble compound containing the anion required on some metal and then placing the electrode thus prepared into a solution of the same anion.

Reversible cells may consist of any combination of electrodes. A reversible cell may be defined as a cell which can be restored to its original condition by an expenditure of electrical energy equal to the maximum electrical energy obtainable from it at constant temperature. An irreversible cell is one in which the original condition cannot be restored by reversing the direction of the current flow; for

instance, the original voltaic pile, made of zinc, sulphuric acid, and silver, is of this type. The water voltameter is another illustration of an irreversible cell. Cells of this kind, as a rule, furnish a rather high electromotive force at the start; this, however, depreciates as the action proceeds, for the electrodes suffer polarization. Reversible cells, on the other hand, yield a current almost constant in electromotive force as long as they continue in action, for in these the electrodes do not suffer polarization.

If the electromotive force of a cell is determined, the voltage represents the difference of potential between the electrodes. Whenever there is a contact of dissimilar substances electromotive force appears, but it is only the electromotive force caused by the contact between the metal electrodes and the electrolyte in which they respectively are immersed, that here calls for comment. To this value the term electrode-potential is given; it represents the work expended in conveying the unit quantity of electricity between electrode and electrolyte.

An explanation of this action was first suggested by Nernst,* who showed that the process might be conceived of as an osmotic process by ascribing to each metal the property of forcing electrically charged particles, ions, into a liquid with which the metal is in contact. This forcing of the ions into the liquid takes place with a pressure peculiar to each metal and is invariable at constant temperature. The metal may thus be regarded as a sort of reservoir of ions wherein these ions are stored under a greater or less pressure, and this pressure is designated as the electrolytic solution pressure of the metal.

Whenever electrical energy is developed, both positive and negative electricity come simultaneously into existence. In the metallic electrodes as such, the particles are without electric charges; at the instant, however, that a particle

Zeitschrift Phys. Chemie, 1889, Vol. 4, p. 129.

passes from an electrode into an electrolytic solution the particle assumes a positive charge and thus becomes an ion; at the same instance the metallic electrode acquires a negative charge of equal intensity. Each additional ion which enters into the solution increases the positive charge of the solution while the electrode becomes correspondingly more and more charged with negative electricity.

Electric charges of opposite sign attract one another and one can thus conceive of a layer of positively charged ions held in attraction by a negatively charged electrode, a difference in potential being thus established. The electrostatic attraction of this layer opposes the tendency of the electrolytic solution pressure of the electrode to force more ions into the solution, and when these counterforces are in equilibrium the action comes to a halt. As the electric charges carried by the ions are very great, such equilibrium is established even when but a few ions have passed from the electrode into the solution.

If a metallic electrode be immersed in a solution of one of its own salts, the metallic ions therein will — by osmotic pressure — oppose the admission of more ions of their own kind. If this osmotic pressure of the ions in the solution is exactly in equilibrium with the solution pressure of the electrode, no ions will be projected from the latter into the solution, and the electrode will therefore not be charged with negative electricity.

On the other hand, if the osmotic pressure is greater than the electrolytic solution pressure, the metallic ions are driven from the solution on to the electrode and the electrode is thereby charged with positive electricity. The solution losing some of its positively charged ions while its content of negatively charged anions is not decreased, becomes negatively charged; the electrostatic difference is thus continuously increased until it counterbalances the osmotic pressure, and then equilibrium is restored.

The electromotive force of a cell can be calculated from the osmotic pressure of the solutions about the electrodes, for, if a substance is allowed to pass isothermally from one condition into another it is immaterial how such a transformation occurs, whether osmotically or electrically.

Knowing the maximum amount of external work which a process can accomplish in an isothermal transformation, the problem is a simple one, for the work which can be done by ions in passing from a given osmotic pressure to another can be transformed without loss into electrical energy.

The fundamental formula by which the electromotive force of an element is calculated from the osmotic pressure of the solutions about the electrodes, is:

$$P = \frac{RTln\frac{p_1}{p_2}}{rE_0}.$$

In this formula

P = potential,
r = valence of the ions,
E_0 = quantity of electricity,
$RTln\frac{p_1}{p_2}$ = amount of energy transformed into work in a gas which expands isothermally from a pressure p_1 to a pressure p_2.

This last formula also holds for a solution which passes isothermally from one osmotic pressure to another.

In a Daniell cell the difference in potential between the two electrodes is practically 1.1 volts. Of this, 0.5 volt is the potential difference between the zinc electrode and the zinc sulphate solution — the electrolyte in which it is immersed, and the balance, 0.6 volt, is the potential difference between the copper electrode and the solution of copper sulphate in which this electrode is immersed.

The term electro-affinity is used to designate the electrode potential in solutions which contain 1 gram-equivalent per liter of the ion given off by the electrode; solutions of this concentration are called normal solutions. An electrode is either positive or negative to a normal solution of its ions, and its electro-affinity is, by the majority of writers, denoted accordingly as positive or negative. The electromotive force of a cell whose electrodes are reversible with respect to any ion, is the algebraic difference between the electro-affinities of the two ions.

In normal solutions the electrode-potential increases for cathions and decreases for anions with the concentration of the electrolyte. In other words, the electrode potential is determined by the concentration of that part of the electrolyte in actual contact with the electrode. It is therefore important that the electrolyte be kept in motion by a stirrer, or, that the electrode be kept revolving in the solution, for by these means the concentration of a solution is kept fairly uniform and an even deposition of the metal precipitated by the electric current is secured. If some precaution be not taken to secure a uniform concentration of the solution, the concentration of the electrolyte about the cathode will decrease and, in consequence, the electrode-potential of the cathode will be lowered, while the concentration of the electrolyte at the anode will be increased, and the electrode-potential of the anode will be raised in consequence. When this occurs, a fall of potential results, indicative of the work done in bringing about these differences in concentration. This phenomenon is known as concentration polarization; it occurs whenever any perceptible amount of chemical action is taking place.

The dissociation voltages previously discussed are, of course, to be considered only as minimum voltages based upon the assumption that the electrolytic process takes place slowly and with weak currents. Heavier currents invariably cause

concentration polarization, and to overcome this higher voltages are required.

The electrode-potential of an ion depends upon its chemical nature and upon the amount in which this ion is present in an electrolyte. If, therefore, more than one kind of cathion is present in an electrolyte, that cathion will be first discharged which has the greater electrode-potential. Through such discharge, however, its concentration will be decreased and thereby its electrode-potential will be lowered; when the electrode-potential of both cathions is identical, both will be discharged simultaneously.

If there are two anions present in an electrolyte, that anion having the lower potential will be the first to be discharged; through this its concentration will be reduced and its electrode-potential will be raised. When both anions have attained to the same electrode-potential they will suffer simultaneous discharge.

These facts explain why the current density — the quotient obtained by dividing the current strength by the electrode surface, and generally expressed in terms of amperes per 100 square centimeters of electrode surface — plays so important a part in electrolysis.

Entirely distinct from concentration polarization is the phenomenon termed chemical polarization. This is due to some new chemical substance or substances formed by the electric current and the consequent substitution of new electrode surfaces for those electrode surfaces with which the electrolytic operation was begun. Thus, in the electrolysis of water the gases liberated by the action of the electric current, hydrogen and oxygen, have a great tendency to polarize the electrode surfaces chemically.

Such a polarization produces a back-pressure, a reverse electromotive force, which, at times, diminishes the effective electromotive force very materially.

The amount of such back-pressure can be practically

measured by first reading the voltage across the two electrodes as usual, then turning off the current and noting the position at which the indicator in the voltmeter halts for a brief space of time ere it travels on to zero. That point where it halts marks the polarization voltage.

If, for instance, the full working voltage in an experiment be 5 volts, the halting-point be at 3 volts, and the amperage 3.5, then the resistance of the cell, *i.e.*, the reverse electromotive force of the cell is:

$$R = \frac{5-3}{3.5} = \frac{2}{3.5} = 0.57 \text{ ohms.}$$

A means of overcoming chemical polarization is the placing of the anode in a solution of a salt of the metal of which the anode is made, or the use of an oxidizing agent, a so-called depolarizer, which oxidizes the product of electrolysis that would otherwise polarize the electrode.

Sources of Current. — In choosing a source for current supply for analytical purposes, the great consideration is the securing of a current which shall have sufficient strength (amperage) and which shall possess a potential (voltage) as constant as possible.

Use can be made of primary batteries (cells), of thermopiles, dynamos, accumulators, and of a direct lighting current.

Generally speaking, electrical elements, or cells, are devices for carrying on electrochemical reactions. Cells which yield an electrical current are called voltaic cells. These can be made to serve as sources of supply, but are open to several objections. Some yield too weak a current, having an internal resistance which is too high; others polarize too rapidly, and this, of course, causes a rapid falling off in current; others again emit noxious fumes and vapors.

If cells are to be used possibly the best is the Edison

Primary battery, or the Daniell cell. The latter consists of

$$Zn : ZnSO_4 : Cu : CuSO_4$$

The Bunsen cell is made of—

$$Zn : ZnSO_4 : C : HNO_3 .$$

In this cell, the carbon, gas-carbon, or graphite, dips into nitric acid which is contained in a cup or cylinder of porous earthenware or clay. The zinc is generally well amalgamated to avoid local currents which are very destructive to the electrode. The chromic acid cell is a modification of the Bunsen cell; it contains potassium dichromate as a depolarizer — the positive pole is carbon, the negative pole is zinc, well amalgamated.

Cells can be grouped for a high electromotive force or for an increased quantity of current.

To obtain a high electromotive force the cells should be linked in series, that is, the positive pole of one cell should be linked to the negative pole of another cell; zincs, for instance, to carbons. The total electromotive force of a set of cells thus linked in series is equal to the voltage of an individual cell multiplied by the number of cells so linked. By thus linking in series, the internal resistance of the system is, of course, also increased.

To increase the quantity of electric current cells must be linked in parallel, that is, all the positive poles are joined together, and all the negative poles are joined together. This arrangement decreases the internal resistance; the total internal resistance of a system linked in parallel is equal to the resistance of an individual cell divided by the total number of cells so linked. Linking in parallel practically amounts to a summation of all of the electrode surfaces.

Of course, if sufficient cells are available, they can be divided into groups and linked partly in series, and partly in parallel. The best current-yield is obtained by linking the cells in

such a way as to equalize, as nearly as may be, the external and the internal resistance.

Thermopiles are practically feasible only in connection with accumulators, for thermopiles do not furnish sufficient current for analytical use. Dynamos can be constructed for every desired current strength and potential.

A direct lighting current will be found very practical, especially so if used with a lamp-resistance arrangement, which will be described later. Among the most convenient devices affording a reliable current supply are accumulators, which can be charged from a lighting system. Accumulators yield a very steady current and almost any amperage desired can be secured by an adjustment of their electrode surfaces.

An accumulator may be defined as a device wherein electrical energy can be stored in the form of chemical energy and from which electrical energy can again be secured at will. As a matter of fact, every reversible cell may be regarded as an accumulator, in practice, however, lead accumulators are almost the only ones used. Planté, in 1860, built the first battery of this kind.

Accumulators of this type consist of two plates of lead coated with a layer of oxide or of sulphate of lead immersed in a 20 per cent solution of sulphuric acid. On passing an electric current through such a cell, that is to say, while charging such an accumulator, the lead anode becomes coated with a layer of lead peroxide, or of lead hydrate, while the cathode receives a coating of spongy metallic lead. On the discharge of the accumulator, both of these layers on the two electrodes, the lead peroxide, or hydrate, on the anode, and the spongy lead on the cathode, are again transformed into lead sulphate.

Streintz states the chemical equation of this change to be:

$$PbO_2 + 2\,H_2SO_4 aq. + Pb =$$
$$2\,PbSO_4 + 2\,H_2O + aq. + 87{,}000 \text{ calories.}$$

M. Le Blanc, in 1895, was the first to give an explanation, by means of the theory of electrolytic dissociation, of the reactions taking place in an accumulator. According to his views, the chief source of the electromotive force of a lead accumulator is the transformation of tetravalent lead ions (from the PbO_2 in water) into divalent lead ions. The solid lead superoxide replenishes the tetravalent lead ions which are consumed, and the divalent lead ions which thus appear enter into chemical combination with the sulphuric acid present, forming sulphate of lead. At the cathode the metallic lead is transformed into divalent lead ions, and these also combine with sulphuric acid to form solid sulphate of lead.

The new Edison storage-battery consists of a nickel peroxide (NiO_2) anode and an iron cathode; caustic potash (KOH) is the electrolyte used.

The electromotive force of this accumulator is low, about 1.1 discharge voltage, but it has certain advantages, for instance, a good storage capacity per unit of mass, a pronounced stability, and moreover, it can be quickly charged and discharged without injury to the plates.*

Pole-papers. — Whatever the source of current, pole-papers so-called, are a convenient means for ascertaining at once which is the positive and which is the negative pole in a given circuit.

These pole-papers are small strips of filter paper charged with a solution of some salt and with a solution of some indicator which instantly indicates an ionic change in the salt used, solutions of sodium sulphate, and of phenolphthalein, for instance.

When a piece of filter-paper moistened with the above solutions is touched by the terminal wires conducting an

* Confer: Roeber E. F., *Elec. World and Engineer*, 1901. Schoop, M. M., *Electro-chem. Ind.*, 1904, and *Sc. Am. Suppl.*, 1905, p. 25064.

electric current, the wires being held but a small distance apart, a pink mark soon appears at the point where the negative pole of the circuit touches the paper, the color being due to the reaction of the phenolphthalein with the alkali which is set free at the cathode.

Current Measurement. — Exact measurements of the working current conditions, of amperage and voltage, are, of course, most essential in electrochemical work. Besides a voltameter, which can be used to measure current strength but which is principally serviceable in checking other measuring instruments, an ammeter and a voltmeter are required.

There are various kinds of ammeters. In the electromagnetic type, an electric current is sent through a coil of wire which surrounds an easily movable core of iron. This iron core is in connection with a pointer which moves across a dial, and the deflection of this pointer indicates the strength of the current which passes through the coil.

The hot-wire ammeter depends for its action upon the heating by the electric current of a very fine wire. This wire is fastened at two points and at its middle is connected to another fine wire which passes around a small drum bearing a pointer. A spring, while at normal temperature, keeps the latter wire in a state of constant tension; when, however, a current is sent through the first wire this becomes heated and slackens, the spring draws on the second wire and thus drum and pointer are set in motion. On account of its having a low internal resistance an ammeter can be placed anywhere directly in the circuit.

Voltmeters are analogous in construction to ammeters; they may be of the electromagnetic or of the hot-wire type. If of the former description, the high resistance needed is secured by the use of a great number of windings of very fine wire, which reduces the consumption of current to a minimum. In the hot-wire type the required resistance is obtained by introducing in series with the instrument the

requisite number of resistance coils; the greater the voltage to be measured, the more of these coils — generally made of very fine wire — are required. Voltmeters, having a very high resistance, are always placed in a shunt-circuit, the latter receiving only a small fraction of the current which flows along the main line.

The resistance of a wire is directly porportional to its length and inversely proportional to its cross-section.

If two paths are offered an electric current and both of these paths have the same resistance, 50 per cent of the current travels by each wire. If, however, a given wire, let us say, wire A, has a resistance of 10 ohms, and wire B has a resistance of 100 ohms, then 10 per cent of the current will pass through wire B, and 90 per cent through wire A.

A voltmeter can also be conveniently used as an amperemeter provided that a known resistance is introduced into the electric circuit and that the terminals of the voltmeter are attached to this resistance.

As,
$$E = CR,$$
$$C = \frac{E}{R},$$

hence, if R is known and E is ascertained by a voltmeter, C can be determined at a glance.

If a resistance of 1 ohm is used in the circuit, the values indicated by the voltmeter read directly in amperes, for

$$1 \text{ ampere} = \frac{1 \text{ volt}}{1 \text{ ohm}}.$$

If the resistance introduced is 0.1 ohm, then each unit indication of the voltmeter represents 10 amperes, for

$$10 \text{ amperes} = \frac{1 \text{ volt}}{0.1 \text{ ohm}}.$$

If the resistance employed is 10 ohms, each unit indication in the scale represents 0.1 ampere, for

$$0.1 \text{ ampere} = \frac{1 \text{ volt}}{10 \text{ ohms}}.$$

It is therefore possible, by the proper selection of resistance, to obtain a very wide range of current strength.

Current Regulation. — The regulation of an electrical current used for electrolytical purposes can be achieved by the introduction of the proper amount of resistance into the circuit, and by a regulation of the distance between the electrodes in the electrolyte.

The so-called resistance boxes usually consist of coils or spirals made of German-silver wire, or of some other alloy. Among alloys specifically made for this purpose are nickeline, constantan, platinoid, and manganin. Manganin is an alloy of manganese, nickel and copper; it has a very high resistance and a very small, negative coefficient of temperature, and it is therefore especially valuable for the manufacture of electrical apparatus, where constancy of resistance at various temperatures is called for.

A current passing through a wire heats the wire, and in consequence the resistance rises. For some purposes it is very desirable to avoid such a variation in the resistance, and in such instances use can be made to advantage of an alloy that has a low temperature coefficient.

Platinoid is an alloy of this description; its increased resistance through a range of 100° C. (from 0° to 100° C.) is only 2.09 per cent, whereas silver, annealed or hard-drawn, shows a rise of 40 per cent, and annealed copper a rise of almost 43 per cent.

Another simple and serviceable device for introducing resistance into an electric circuit is the lamp-bank.* A lamp-

* Consult Hopkins, *liber. cit.*, p. 13.

bank is made by arranging a number of lamp-sockets partly in parallel, partly in series, upon a slab of slate or marble, and then inserting the necessary number of lamps properly grouped to give the desired resistance. The current may be conveniently taken from a direct lighting circuit.

When lamps are arranged in parallel, their combined resistance is equal to the resistance of one lamp divided by the number of lamps in parallel; when arranged in series their combined resistance is equal to the resistance of one lamp multiplied by the number of lamps in series.

Assume, for instance, that eight 16 candle-power lamps are available and that the lamp-board is arranged in such a manner that these lamps can be used either in parallel or in series.

Let $E = 110$ volts,
$R = 220$ ohms,

and have the 8 lamps arranged in parallel.

$$C = \frac{E}{R},$$

therefore, in this instance,

$$C = \frac{110}{220} \times 8 = 4.0,$$

i.e., 4 amperes would pass through the lamps thus grouped.

If the 8 lamps were arranged in series,

$$C = \frac{110}{220 \times 8} = \frac{110}{1760} = 0.062.$$

i.e., only 0.062 ampere would flow through the combination.

It is thus evident, that by grouping some of the lamps in parallel and some in series, and by using lamps of different resistances, almost any desired amperage may be secured.

Of course, the introduction of resistance into the circuit in such a manner is the reverse of economical; a 110-volt

current cut down to, say, 4 volts, renders no more effective service than the current of a 4-volt generator directly applied. The actual current strength in any electrolytic circuit is determined by the formula:

$$C = \frac{E - e}{R + R_1}$$

in which:

E = voltage of the current,
e = counter-voltage,
R = resistance of cell,
R_1 = resistance of the conductor (the leads), between generator and cell.

In electrochemical analysis, however, the voltage is generally measured directly between the terminals of the cell, that is, the value of R only is sought and the value R_1 not taken into account.

The resistance of an electrolytic cell may also be calculated by the formula:

$$R = \frac{D\,\rho}{E.S}$$

in which,

D = distance, in centimeters, between the electrodes — these being assumed to be perfectly parallel,
ρ = the specific resistance of the electrolyte,
$E.S.$ = electrode surface, *i.e.*, the area in square centimeters of each electrode.

If there are three plates and the current flows from the central plate to each of the other two, then the value of R is found as above for either side, and the combined resistance equals one-half of the value thus found.

The resistance of electrolytes varies with their chemical nature, with their concentration, and with the temperature. An increase in temperature markedly decreases the resist-

ance of electrolytes; in this respect electrolytes resemble the behavior of carbon.

The cross-section of a wire, in square millimeters, for instance, of a copper wire used for conducting an electric current, is calculated by the formula:

$$C.S. = \frac{L.C.\ 0.01687}{D.P.},$$

in which:

$C.S.$ = cross-section in square millimeters,

L = total length of conducting wire — that is, the sum of the lengths of wire leading from the source of current supply and back,

C = the maximum current strength to be conducted — expressed in amperes,

$D.P.$ = the maximum permissible drop in potential — expressed in volts,

0.01687 = specific resistance of copper, *i.e.*, the resistance of a copper wire 1 meter long and 1 square millimeter in cross-section.

The cross-sections of round wires are very often given in circular mils. A mil is the one-thousandth part of an inch (= 0.0254 millimeter). A circular mil is the area of a circle the diameter of which is one mil; a circle having a diameter d has an area of d^2 circular units. One circular mil is equal to 0.000506709 square millimeter, and one square millimeter is equal to 1973.52 circular mils.

In calculating the cross-sections of the conducting wires between the sources of supply and the working-station a safety-margin of from 20 to 25 per cent over and above the amount calculated, should be allowed.

Electrodes. — The electrodes used in electro-analytical work are usually made of platinum. The cathode may, according to conditions, be either a crucible, a dish, a flag or foil, a cone, or a cylinder.

If a dish be used it is generally selected to hold from 150 to 200 cubic centimeters; whatever the shape chosen, the utmost care must be taken to have the surface which is to receive the electrolytic deposit perfectly smooth and absolutely clean and bright, above all, not a trace of oil or of any other fatty matter may be present.

The anode may be a plain foil or a flag, a wire to the end of which a small disk has been soldered, a spiral coil, or a cylinder. To whichever shape preference is to be given will, to a certain extent, be determined by the current density required.

A convenient electrode support consists of an upright rod or bar of glass to which a metallic ring and a metallic bar are attached in such a way that these can readily be set in any position desired. The metallic ring is intended for the support of the cathode — a platinum dish for instance — and is in connection with the negative pole of the current. The anode is fastened to the metal bar and this is connected with the positive pole of the electric current.

As warm electrolytes are superior conductors, the platinum dish, which serves as the cathode, may conveniently be placed on a thin plate of asbestos and heated by a small gas-flame, electrically, or in some other manner. Various analyses, of course, demand various temperature conditions, but it seems that, as a rule, 50° C. should not be exceeded.

The use of a stationary anode generally entails the employment of a weak current and hence necessitates the use of considerable time for the electrodeposition of some metals. This is due to the fact that concentration changes are set up in the solution, a decrease in the concentration of the cathions becoming noticeable near the cathode as the deposition progresses. This difficulty can be avoided by the use of a rotating anode driven by an electric or water motor and revolving perhaps from 30 to 130 times per minute. By this means the concentration of the electrolyte is kept uni-

form, a stronger current can be employed, and, in consequence, considerable time be saved.

It is also possible to make use of a rotating cathode, a platinum crucible, for instance, answers this purpose well.* Giving such a cathode a speed of rotation of from 600 to 700 revolutions per minute, and working with a normal current density of from 5.0 to 6.6 amperes, 15 to 30 minutes will suffice for an electrodeposition which ordinarily would require hours for its completion.

In calculating electrode areas it is customary to measure the surfaces of the electrodes only to the extent that the same are in contact with the electrolyte.

Formulæ for Calculation of Electrode Areas.

d = diameter, $\pi = 3.1416$.
r = radius.

Circumference of a circle: $d \times \pi$,
$r \times 2\pi$,
Area of a circle: $d^2 \times .7854$,
$r^2\pi$.

Surface areas.

1. Foil or flag: Height × length.
2. Cone or pyramid: Product of perimeter of base by half the slant height, plus the area of the base.
3. Open-end cylinder or prism: Perimeter of one end × height.
4. Closed-end cylinder or prism: Perimeter of one end × height, plus twice the area of one end.
5. Interior surface of a dish (curve-surface of a segment or a zone of a sphere): Diameter of sphere × height of segment or zone × π.

* *Am. Journal of Science*, Vol. 15, p. 320.

6. Cylindrical gauze: $\pi d^2 \sqrt{nlb}$.*

d = diameter of wire,
n = number of meshes per square centimeter,
l = length, b = width } of gauze used.

Current Density. — This term, as previously stated, designates the ratio of the electrode area to the flow of current. It is customary to term the current strength per 100 $\overline{\text{cm}^2}$. (one square decimeter, 1 dm^2) of electrode surface, the *normal density* of current, and this value is symbolized by $N.D._{100}$.

For instance, $N.D._{100} = 0.5$ signifies that the current flow for every 100 square centimeters of electrode surface is 0.5 ampere.

Let, D = current density,
C = current strength,
$E.S.$ = electrode surface on which electro-deposition takes place.

then,
$$D = \frac{C}{E.S.},$$

and
$$N.D._{100} = \frac{C}{\left(\frac{E.S.}{100}\right)}.$$

If the $N.D._{100}$ and the electrode surface are known, the current strength is readily calculated by the formula,

$$C = N.D._{100} \times \frac{E.S.}{100}.$$

For instance, let:

C = 5 amperes,
$E.S.$ = 180 $\overline{\text{cm.}^2}$.

* Winkler : *Berichte*, Vol. 32, p. 2192.

Then: $$D = \frac{5}{180} = 0.028,$$

and, $$N.D._{100} = 5 \div \frac{180}{100} = 2.8.$$

and, $$C = 2.8 \times \frac{180}{100} = 5.0.$$

The current density may either be the same or unlike at the two electrodes. If both electrode areas are alike, a given current strength will, of course, ensure identical current density at both electrodes. A given current strength passing from a small electrode area naturally means a high current density at that electrode. Thus let:

$$C = 5.0$$
$$E.S. = 1.0$$

then, $$D = \frac{5}{1} = 5.0$$

The same current strength passing form a large electrode surface determines a low current density at that electrode.

Thus: $$C = 5,$$
$$E.S. = 100,$$

$$D = \frac{5}{100} = 0.05.$$

All electrochemical operations are greatly influenced by the current density.

Records. — The records of all electrochemical work should be kept in such a manner as to permit of the exact repetition of such work at any time. What the specific data of such record should be, is, of course, in a large measure determined by the nature of the work under consideration.

In all cases, however, such record should include data of the source of the current used, the time during which the current passes, the material of which the electrodes consist, the distance between the electrodes in the working-cell, the active area of the electrodes, the voltage and amperage employed, the current density, the character of the electrolyte, its temperature throughout the reaction, and, in addition, any specific phenomena which may be noticed at anode and cathode.

Resumé.—The principal facts to be borne in mind in electro-analytical work and in the study of electrolytic processes are the following:

Each ion bears a definite charge of electricity. The ionic charge for a monovalent gram ion is = 96,540 coulombs. The ionic charge is directly proportional to the valence of the ion and is the same for all ions of the same valence, whether such an ion be an individual ion or a complex ion. Thus, the cathions silver and sodium bear equal charges of positive electricity, while the anions, chlorine, iodine, and NO_3 bear equal charges of negative electricity.

The amount of an element deposited or liberated electrolytically is proportionate to the current used. A given current will deposit or set free of various elements, amounts directly proportionate to the atomic weights of those elements and inversely proportionate to their valence.

Thus, taking the atomic weight of silver, 107.93, as the basis, the number of grams of any element set free or deposited by one ampere hour is equal to:

$$0.037291 \times \frac{\text{atomic weight}}{\text{change of valency}}.$$

For instance, of copper there will be deposited from a solution of cupric chloride, $CuCl_2$:

$$0.037291 \times \frac{63.6}{2}$$

$$0.037291 \times 31.8 = 1.1858 \text{ grams.}$$

One ampere hour will thus deposit of:

Silver, . . . 4.0248 grams,

Copper (from a cupric salt) 1.1858 grams,

and these values are in the same ratio as the respective chemical equivalents of silver $\frac{(107.93)}{1}$ and of copper $\frac{(63.6)}{2}$ *i.e.* as 107.93 and 31.8.

Great stress must also be laid on having the current used sufficient in amount, in other words, the current density must be sufficiently large so that the rate at which a metal is precipitated is greater than the rate at which it tends to redissolve in the solution from which it is being deposited. This is proportionate to the area of the surface of the electrode at which the deposition occurs, hence the amount of current per unit of surface area, the current density, is a factor of prime importance.

While the various chemical elements are set free in equivalent amounts at the electrodes, it is necessary to remember that the amount of electrical energy requisite to effect an electrolytic decomposition varies with the nature of the chemical combination to be decomposed.

The minimum dissociation voltage, the critical voltage, differs for each element and is characteristic of it. Advantage is taken of this fact to separate different metals analytically. For instance, in passing a current through a solution of several metals, the metal having the lowest critical voltage will be deposited first; if the voltage be then increased, metal after metal will be precipitated, and the metal having the highest critical voltage will be the last one to be deposited.

As a rule, thermal units are employed to measure the energy evolved or absorbed in the formation of chemical compounds. As previously stated, the thermal units employed are either calories, or, Calories, the former representing the amount of heat needed to raise the temperature of one gram of water one degree C., from 15° C. to 16° C.; the latter, the amount of heat needed to raise the temperature of one kilogram of water one degree Centigrade.*

To effect an electrolytic deposition of a chemical substance in aqueous solutions, an amount of electrical energy must be used equivalent to the number of calories involved in the formation of the compound to be electrolysed.

The unit of electrical energy is the joule; one joule is equivalent to, practically, 0.24 calorie, or to 0.00024 Calorie. When the heat of formation of an electrolyte is known, this value divided by 0.24 equals the joules required to effect its electrolysis.

1 joule = 1 coulomb × 1 volt, therefore, the number of joules divided by 96,540 — or a multiple thereof — represents the critical voltage, *i.e.* the minimum voltage necessary to effect the desired electrolysis.

The fundamental facts then to be remembered are, that it always requires a definite quantity of energy to effect the electrolysis of a given substance at a given temperature, and that such electrolysis can only be effected by the use of a definite minimum voltage.

In passing upon the efficiency of any electrolytic process, it is necessary to pay due regard to both current efficiency and to energy efficiency. In other words, it is necessary to determine how closely the weight of the product obtained, compares with the weight of the product theoretically producible by the number of coulombs used; furthermore, the weight of the product obtained should be compared with

* Confer: Joseph W. Richards' "Electrochemical Calculations," *Journal Franklin Institute*, 1906, p. 131.

the amount theoretically obtainable by a perfect utilization of the total number of joules employed.

Thus, if the current efficiency in a given process is 90% and the voltage efficiency is 60%, then the energy efficiency is

$$= \frac{90 \times 60}{100 \times 100} = 54\%.$$

In obtaining the electrodeposition of an element from a compound, it is a great advantage to effect such electrodeposition from an *ous*-salt rather than from an *ic*-salt for the reason that the *ous* compound compared with the *ic* compound, contains twice the amount of the metallic constituent per unit weight of the non-metalic radicle with which it is combined. In consequence an electric current of a given amperage will deposit twice as much metal from an *ous* salt as it will from an *ic* salt, and although a somewhat higher voltage is required in the former case, this is more than compensated for by the increased output obtained.

CHAPTER VI.

ELECTROTECHNOLOGY.

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Introduction. — The applications of electrochemistry are so numerous that it will be desirable to devise some sort of a classification in order to gain a general survey of the subject.

In so doing, two principal groups may be established:

I. Direct action processes.

II. Indirect action processes.

In the first of these groups there must be counted all processes in which the electric current acts directly; in the second, all processes in which the electric energy suffers partial or entire transformation into some other form of energy before being applied to the work required. The first group would thus embrace all processes of electrodeposition from solutions — metals and non-metals; the second group would

include electrodeposition from fused electrolytes, and all electrothermic processes.

For the sake of convenience, the following sub-divisions can be made:

A. Electro-inorganic Processes.
  I. Direct Action Processes.
    Electrodeposition from solution.
    Electroplating.
    Chlorine and Alkali-hydrates.
  II. Indirect Action Processes.
    Electrodeposition from fused electrolytes.
    Electrothermic processes.

B. Electro-organic processes.
  I. Direct action processes.
  II. Silent discharge processes.
  III. Electro-osmosis.

A. I. DIRECT ACTION PROCESSES.

Electrodeposition from Solution.

Copper. — Although several processes have been devised for obtaining copper from its ores by the aid of the electric current, not one of these processes has attained to any great importance in commercial practice.

In one of the earliest of these processes, that devised by Marchese in 1884, the ore was prepared and brought into the form of an impure sulphide, consisting of copper, lead, and iron. This compound was cast into anodes and subjected to electrolysis in a sulphuric acid solution.

In later processes solvents are used to extract the copper from its ore, and the solutions thus obtained are subjected to electrolysis, insoluble anodes being employed.

Thus, in the Siemens-Halske process the solvent employed for extracting the copper present as sulphide, is an aqueous

solution of ferric sulphate. In effecting the extraction of the copper this ferric sulphate becomes reduced to the ferrous condition, but is, in turn, restored to its original condition by undergoing oxidation in the anode section of the trough after the metallic copper has been precipitated from its sulphuric acid solution at the cathode. Carbon anodes are generally used.

In the Hoepfner process, the ore is not subjected to any preliminary roasting; the copper, in the form of cuprous sulphide, is leached out by means of a sodium chloride solution containing cupric chloride, cuprous chloride is thus formed and is kept in solution by means of the sodium chloride which is present. The electrolytic troughs are separated into anode and cathode chambers by means of diaphragms and the electrolyte is first passed through the cathode chambers where most of the copper is precipitated. In the anode chamber the remaining cuprous chloride is changed to the cupric form, and the process is thus made a continuous one.

While the extraction of copper from its ores by electrolytic action is as yet not well developed, the electrolytic refining of copper is one of the most important, if not the most important, application of electrochemistry.

The first suggestion of electrolytic copper winning is credited to Becquerel (1836); the first obtaining of electrolytic copper on the commercial scale to James B. Elkington of England (1865).

Two systems are employed in copper refining, the series system and the multiple system; the latter is the older.

In the multiple system each anode is connected with the conductor from the positive pole of the electric current; each cathode with the conductor from the negative pole.

In the series system, due to E. S. Hayden of Connecticut, only one end-anode in each tank is connected with the positive pole and at the opposite end only one cathode is connected with the negative pole. Between these electrodes,

copper plates are set in an upright position; the circulation of the electrolyte may be maintained by compressed air or by some other device.

The plates of crude copper which serve as anodes, usually have a surface of from 55 to 75 square decimeters, and are from 2 centimeters to 4 centimeters thick; the cathodes consist of thin plates or foils of pure copper. The distance between the electrodes is generally maintained at from 2.5 to 5.0 centimeters, the electrolyte used is a solution of sulphate of copper acidified with sulphuric acid. The voltage employed is low, probably not exceeding one-half volt.

In preparing the electrolyte, copper sulphate solution and sulphuric acid, care must be taken to insure a solution rich in copper, and to have it contain sufficient sulphuric acid to prevent the formation of hydrated cupric oxide; on the other hand, care must be taken to guard against an excess of sulphuric acid, as this would cause the liberation of hydrogen at the cathode in the place of copper. The temperature of the electrolyte is advantageously held at about 33° C. to 37° C.

The question of current density is of course a very important one, the value of ND_{100} ranges from 1.3 to possibly as high as 4.00. However, too high a current density must be avoided, as this causes the copper to be deposited in uneven masses, possessing but poor coherence.*

The tanks in which the electrolytic deposition takes place are generally lined with lead; there are often several hundred of these in a plant. When in the course of operation the anodes have been reduced to thin sheets, the process is interrupted, the anodes are removed and re-smelted, the cathodes are likewise removed and recast, and the anode-slime, or mud, as it is termed, is subjected to separate treatment for the obtainment of the precious metals which occur therein whenever such are present in the copper ores worked.

* Consult: S. Cowper-Coles, *Trans. Faraday Society*, 1905, p. 215, and L. Addicks, *Journal Franklin Inst.*, 1905, p. 421.

Among the impurities frequently found associated with copper are iron, cobalt, nickel, zinc, gold, platinum, silver, bismuth, antimony, arsenic, and lead. Of these impurities iron, cobalt, nickel, and zinc dissolve in the electrolyte, but are not apt to be precipitated on the cathode under the current conditions employed for the electrolytic deposition of the copper.

Among the impurities found in the anode-slime are gold and silver. In some copper ores the amount of these metals recovered from the anode-slime is very considerable. For instance, an analysis given by E. Keller* shows the amount of the precious metals contained in an anode-slime derived from a copper ore mined near Butte, Montana, to have been as high as 0.2% to 0.3% of gold and 53% to 55% of silver.

The purity of copper electrolytically refined is very high, frequently ranging up to 99.95% and 99.99%.

To illustrate the manner in which the output of an electrolytic copper refining plant can be calculated, assume that the normal current-density employed is one ampere per square decimeter, *i.e.*, $ND_{100} = 1.00$. Further, assume that the active anode surface in one vat is 372 square decimeters, then each vat requires 372 amperes.

The weight, in milligrams, of any element set free by one coulomb of electricity is equal to its atomic weight divided by its valence and multiplied by 0.01036, the electrochemical equivalent of hydrogen.

Thus, one coulomb will deposit from a cupric salt solution $\frac{63.6}{2} \times 0.01036 = 0.329448$ milligram, say 0.33 milligram of metallic copper.

One ampere-hour equals 3600 ampere-seconds, hence, one ampere in one hour will deposit $0.33 \times 3600 = 1.188$ grams of copper and in 24 hours $1.188 \times 24 = 28.5120$ grams.

* *Journal of American Chemical Society*, 1897, p. 778.

In the same period 372 amperes will deposit 28.5120 × 372 = 10,606 grams, or, 10.606 kilograms of copper. This amount multiplied by the number of vats in use, will of course give the total output in 24 hours.

As to the question of energy consumption, assume a maximum current efficiency, and assume that the drop in potential is 0.25 volt. Each vat will thus require 0.25 × 372 = 93 watts, and this corresponds to $\frac{93}{746}$ = 0.125 H.P.

One H.P. will therefore deposit in twenty-four hours, 0.125:1.0:: 10.606: x = 84.85 kilograms of copper, and a plant of 5000 H.P. would therefore yield 84.85 × 5000 = 424,250 kg. of copper in twenty-four hours.

Silver. — The principles underlying the process of refining silver electrolytically, and especially adapted to its separation from gold and copper, were worked out by Moebius.

The electrolyte used is a solution of nitrate of silver containing about 1% of silver and from 0.1 to 1% of free nitric acid. The cathodes consist of pure silver foil and these receive a very light coating of oil in order to permit of a more ready removal of the crystals of silver, the form in which the silver separates from the electrolyte under proper current conditions. The anodes are made of crude silver, containing about 95% of this metal, the balance generally consisting of gold, platinum, and copper.

As stated, the silver separates in a crystalline condition and the removal of these crystals is effected by wooden arms which are kept in slow movement, constantly freeing the cathodes from these crystals; if this were not done the crystals would readily grow to the anodes and in this manner of course establish a short circuit. The anodes are inclosed in a sheathing of canvas and in this the anode-slime accumulates. This anode residue is of course separately treated for the recovery of the precious metals it contains.

The current conditions generally employed for the electrolytic refining of silver are, voltage = 1.5 and $ND_{100} = 2.5$.

Gold. — The extraction of crude gold from its ores is generally effected either by the use of mercury, by one of the so-called chlorination processes — wherein chlorine is the active agent, or else by use of potassium-cyanide acting in the presence of atmospheric oxygen.

Potassium-cyanide is the reagent employed in the Siemens-Halske process and the gold is recovered electrolytically from the cyanide solution. The cyanide liquor contains not more than 0.05% of potassium cyanide. The anodes are generally made of iron, although carbon, Acheson-graphite, and lead-per-oxide anodes are also used; they are inclosed in bags of canvas or linen.

The cathodes are made of lead, and when sufficient gold has been deposited on them they are cupeled and the gold obtained. The crude gold thus secured contains about 85% to 90% of pure gold; this is subjected to electrolytic refining while the lead recovered is reduced, recast, and again used for cathodes. The current-de sity employed is very low. ND_{100} ranges from about 0.003 to 0.005; the voltage from about 1.75 to 2.00 volts.

In Wohwill's process for the electrolytic refining of gold the anodes of crude gold are placed into a hot solution of hydrogen auric chloride ($H\ Au\ Cl_4$) containing hydrochloric acid. The cathodes consist of very thin sheets of pure gold. To insure a well adherent cathode-deposit, the temperature is kept at about 70° C.; the electrolyte contains 3% of gold and from 3% to 4% of hydrochloric acid. The voltage employed is about 1 volt, the $ND_{100} = 10$ amperes. The product secured contains from 99.80% to 100% of gold.

Lead. — While there seems to be little opportunity for a commercially profitable process of winning crude lead electrolytically from its ores, the process of refining crude lead electrolytically is well established, one of the chief advan-

tages of such a process being that it permits the obtainment of a pure lead and of a pure bismuth, the latter a common impurity in lead won by metallurgical processes.

In the process of A. G. Betts, lead is obtained electrolytically by dissolving the metal in hydrofluosilicic acid, which gives an electrolyte of lead-silicofluoride from which metallic lead is deposited at the cathode in the form of a dense and smooth deposit. Addition of a trace of gelatine, an organic colloid, to the electrolyte insures the coming down of the electrolytic deposit in a finely crystalline condition. The solution is kept continuously circulating through the vats.

The anodes are crude lead, and are apt to contain as impurities some copper, antimony, bismuth, and silver; these tend to remain in the anode-slime provided the ND_{100} does not exceed 1.0 ampere. If iron, nickel, and zinc are also present these pass into the solution. The voltage employed is about 0.4; the electrolyte is not heated. Starting from a crude lead containing about 95% of the metal, the refined product is practically chemically pure.

Nickel. — The application of electrical energy to the winning of nickel is practically confined to the refining of this metal.

The conditions to be observed in order to deposit nickel successfully from an aqueous solution of its sulphate or its chloride are a temperature of between 60° and 70° C., an electrolyte containing about 3% of nickel together with a trace of free sulphuric acid or hydrochloric acid, a normal current density of from 0.5 to 2.5 and a voltage of from 1 to 2 volts. Generally speaking, the higher the current density the smoother and the brighter the deposit secured.

Electrodeposition of nickel from nickel solutions by means of insoluble anodes is thoroughly practicable. Anodes of lead-peroxide have been used for the purpose; when a sulphate salt of nickel is used as the electrolyte, the sulphuric acid set free in the operation must be neutralized with nickel-hydrate or nickel-carbonate.

The D. H. Browne process, formerly used by the Canadian Copper Company, was worked on an alloy of nickel and copper, containing about 43% of the former and 54% of the latter metal.

This alloy was cast for anodes; some of it was also used as the electrolyte, being treated with chlorine and sodium chloride, which brought these metals into solution as cuprous chloride and as nickel chloride. Most of the copper having been precipitated from this solution by electrolysis, the remainder was thrown down by the action of sodium sulphide, while any iron and cobalt present were precipitated by sodium hydrate and by chlorine.

The solution thus obtained contained practically only nickel chloride and sodium chloride; the latter was removed by concentration and crystallization and the nickel was finally precipitated electrolytically from a hot solution. The voltage employed for this purpose was about 3.5 volts; the anodes used in this operation were made of graphite, suspended in vessels of porous earthenware. The electrolyte after coursing through the vats returned to the evaporators, where it suffered further concentration. The chlorine evolved at the anodes was made to dissolve the copper-nickel alloy used as electrolyte. The nickel won by this process attained to a purity of 99.85%.

Tin. — There is no electrolytic method in use for winning tin from its ores, or for refining it, however, the securing of tin from tin-plate scrap is quite an industry.

Tin plate is sheet iron coated with tin, and although only a thin coating of this metal is used for the purpose, a large amount of tin is consumed in this way. The scrap from which the tin is thus recovered is in part the waste of new tin plate and in part the scrap of old tinned articles.

Several processes have been devised for the recovery of tin from this material. Thus Siemens and Halske employ the scrap as anode, suspending the same in wooden or wicker

baskets; as cathodes they employ copper which has been tinned. In the process chiefly developed by the Goldschmidts in Essen, Germany, the tin-plate scrap, containing about 30% of tin, is placed in iron wire baskets which are suspended, as anodes, in iron vats. The latter are made to serve as cathodes, the electrolyte is a 10% solution of caustic soda. The operation is conducted at a temperature of about 70° C., the voltage employed is 1.5 volts. In the tin thus electrolytically deposited, lead and iron are apt to occur as impurities. The iron from which the tin coating is originally removed is fairly pure and can be reworked.

Tin might also be recovered from lead scrap, that is to say, from sheet lead or from pipes upon which a layer of tin has been rolled; this lead scrap could be made the anode, and sulphuric acid might be employed as the electrolyte. In such a process of course the metallic lead would remain, barring a small percentage of the metal which would be transformed into sulphate, while the tin was recovered.

Zinc. — Electrolytic processes are of great value in the obtainment of zinc from its ores.

In Silesia, Germany, during the last decade of the past century, a process was in use wherein zinc sulphate was used as the electrolyte, the anodes employed being made of lead peroxide; it was, however, ultimately abandoned because it could not compete commercially with other metallurgical processes. Among more recent methods of winning zinc electrolytically from its ores, must be named the Siemens-Halske process, the Ashcroft process, and the Hoepfner processes.

In the Siemens-Halske process, as well as in that of Ashcroft, the ores worked are essentially compounds of lead sulphide and of zinc sulphide, containing approximately 20% of zinc and 30% of lead; the ores are also argentiferous. In one of the processes by Hoepfner the crude material worked was essentially an iron ore containing about 10% of

zinc; the electrolyte used was a solution of zinc chloride, the anodes were made of carbon, the cathodes consisted of revolving zinc plates and the anode and cathode-chambers were separated by diaphragms. The ND_{100} was 4 amperes, the voltage ranged between 3 and 7 volts.

In another Hoepfner process, used in England, the zinc was roasted, secured as an oxide, and then treated with a hot concentrated solution of magnesium chloride in which the oxide of zinc dissolves as a basic salt. This solution received subsequent treatment with carbonic acid gas and with calcium chloride solution, the zinc appearing ultimately as zinc chloride, which solution was submitted to electrolysis. Carbon anodes were used, the $ND_{100} = 1$ ampere and the voltage about 3 volts; the purity of the resulting product was 99.95%.

A process for refining zinc electrolytically has been devised by Roessler and Edelmann. In this method the crude zinc, used for anodes, contains about 20% of impurities, among which should be noted copper, silver, lead, nickel, and cobalt. The $ND_{100} = 0.8$ to 0.9 ampere, the voltage ranges from 1.25 to 1.50, the electrolyte is not heated. From the anode-slime, silver, copper, and lead are recovered by separate processes. In this process also the purity of the refined product is approximately 99.95%.

Electroplating.

Electroplating. — The first electrotechnical process devised seems to have been the electrodeposition of metals, the art of electrotyping. The making of exact metallic reproductions, replicas, of objects was discovered independently by Jacobi, by Spencer, and by Jordan; the first-named of these exhibited electrotype copies of medals before the Academy of St. Petersburg in 1838. Two years later, Murray discovered that non-conducting bodies when coated with graphite would serve equally well as a base for electrodeposi-

tion. From this process of electrotyping, a few years later, the process of electroplating was evolved.

The fundamental difference between the two processes is that in electrotyping the electrolytic deposit is meant to be removed from the surface on which it has been formed, and therefore too firm an adherence of the deposit on the object on which it is made must be avoided; this is effected by giving to the object a preliminary thin coating of oil or of a solution of some salt. In electroplating the deposit is meant to adhere as firmly to the object as if it had been welded on the same; for a successful electroplating absolutely clean surfaces are therefore an essential condition.

While for a long time it has been known that the chemical composition, the concentration, and the temperature of the electrolyte, as well as the current density employed, are all factors of importance if a well-adherent electrodeposit is to be secured, a recent study of the subject by Wilder D. Bancroft,* "On the Chemistry of Electroplating," has thrown light on many aspects of the problem which were but little understood before.

Among other interesting facts Bancroft found that a poor metallic deposit is nearly always caused by the precipitation of some salt of the metal in place of the pure metal, for instance, by the formation of an oxide, a hydro-oxide, or a cyanide. Therefore, the addition of any chemical which will dissolve a salt or which will prevent its formation must improve the quality of the desired electrodeposit.

Maintenance of proper temperature conditions is likewise essential, as is also the rate at which the electrolyte is stirred, for a sufficiently concentrated solution must always be maintained at the cathode; too dilute a solution at the cathode results in the formation of sandy or pulverulent deposits.

Determining the best conditions in individual cases requires considerable care and experimenting, yet the general

* *Journal of the Franklin Institute*, 1905, Vol. 140, p. 139.

principles underlying electroplating are very simple. The object to be plated is put into an electrolyte which is a solution of some salt of the metal with which the plating is to be done. This solution is termed the bath. The object to be plated is attached to a wire leading in from the zinc plate of a primary battery, or from the negative pole of a dynamo; in short, the object to be plated is made the cathode of the bath. The metal with which the object is to be plated is suspended in the bath from another wire which comes from the carbon, or copper electrode of the primary battery, or from the corresponding pole of the dynamo. The metal which is thus to be deposited on the object is termed the anode of the bath.

In general it may be said that the working conditions for electroplating are a low voltage and a fairly strong current. The voltages employed range between 1 and 5 volts, the current densities of course differ considerably for the different metals; some ND_{100} values are:

For gilding, 0.2 ampere,
For silvering, 0.3 to 0.6 ampere,
For nickeling, 0.3 to 0.6 amperes,
For copper plating, 0.4 ampere,
For zinc plating, 1.0 to 3.0 amperes.

A careful study of the conditions necessary to secure a good and well adherent electrodeposit of zinc has been made by Mylius and Fromm.* From this it appears that the best working conditions — when zinc sulphate is employed as the electrolyte — are to have 4 to 6% of zinc in the electrolyte, a ND_{100} = 1 to 3 amperes, and a voltage of from 3 to 4 volts. Above all, it is necessary to suppress as far as possible the liberation of free hydrogen at the cathode, for this causes a basic condition in the electrolyte near the cathode, a condition conductive to the deposition of spongy zinc and inter-

* *Zeitschrift f. Anorg: Chemie*, 1895, p. 144.

fering with the precipitation of a firm, coherent deposit of the metal. The presence of mere traces of some other metals more electronegative than zinc, also tends to the formation of spongy zinc, and such metals should therefore be removed before electrolysis.

Alloys also can be deposited by electroplating; thus it is possible to make an electroplate of brass by using a solution of cyanide of zinc and of cyanide of copper, both dissolved in potassium cyanide. Bronzes, that is to say, alloys of copper and tin, can also be electroplated, the deposition taking place from mixed solutions of their salts. Thus far, however, alloys have not been extensively used in electroplating.

Chlorine and Alkali-Hydrates.

Chlorine and Alkali-Hydrates. — In the electrolytic winning of chlorine and of alkali-hydrates from solutions of alkaline chlorides, the fundamental principle to be observed is the keeping separate of the products produced at the cathode from those produced at the anode. At the cathode, alkali and hydrogen are generated, at the anode, of course, chlorine.

To achieve this holding apart of the products of the reaction, three different kinds of processes have been devised; these may be designated respectively as:

I. The diaphragm process.
II. The bell process.
III. The mercury process.

The chlorine gas which is obtained by these processes is either liquefied and thus made available for shipment, or it is transformed into bleaching powder; the alkali obtained can, of course, be readily turned into the caustic condition. Probably the chief reason why the entire output of caustic alkali needed in the chemical industry is not produced exclu-

sively by electrolytic methods, for these methods are economical, is the fact that there is not a sufficiently large demand for the chlorine which, of course, is simultaneously produced in quantity equivalent to the alkali obtained.

The hydrogen gas which is incidentally produced with the alkali is in many factories allowed to escape unused; in some places it is employed in the manufacture of fuel-gas, and in others it is condensed under pressure and is thus made available for transportation.

The crude chemicals employed in the electrolysis of alkali-chlorides are essentially chloride of potassium, obtained from carnallite and common salt. It is very important that only pure solutions of the alkali-chlorides be used for electrolysis, for appreciable amounts of impurities interfere seriously with the working of the processes and with the quality of the products obtained.

In cases where the products liberated at the two electrodes are not kept separate, and where a free intermixing of the cathode and anode-solutions is allowed, hypochlorites and chlorates will be formed, according to the temperature and the current density employed.

The former salts, that is to say, the hypochlorites, are produced at the anode when a low temperature and a low current density are used; such hypochlorite solutions, practically not exceeding 2 or 3% in strength, are best used on the spot for electrolytic bleaching. The formation of chlorates is, on the other hand, favored by the use of a high current density and the presence of some alkali. Thus, potassium chlorate is now made almost exclusively by electrolysis, about 5 kilowatt-hours being used per kilogram of potassium chlorate produced. If this product is subjected to further electrolytic treatment with a high current density, at a low temperature, potassium per-chlorate results.

I. **Diaphragm Process.** — The principal problem to be solved in processes of this description, is to find a suitable

material which shall prove resistant alike to chlorine and to alkali. In Germany, after a great deal of experimenting, plates of Portland cement were selected for the purpose: in the United States, asbestos is the material generally used.

From the very fact that any material serviceable for diaphragms must be sufficiently porous to permit of the passing of the electric current, it is unavoidable that a part of the hydroxyl ions set free will also pass through, and these, naturally reacting with some of the chlorine which is liberated, will cut down the output of that gas.

Carbon anodes are preferably employed, the working temperature is held at about 85° C., the ND_{100} ranges from about 1 to 2 amperes at the diaphragm. In some processes the alkali-chloride solution is conducted only to the cathode compartment (Griesheim-Electron system), in others the solution of the electrolyte flows from the anode compartment to the cathode compartment (Systems of McDonald, and of Hargreaves and Bird).

II. **Bell Process.** — The fundamental principle of processes of this description is the use of some non-porous, non-conducting medium, which serves to keep separate the solutions at the anode and at the cathode, while it permits those parts of the solution not in contact with the gases set free at the electrodes to intermingle freely.

The bell device consists essentially of a vessel, technically the bell, which is generally an open box made of sheet iron and coated with some non-conducting material. This bell is suspended with the open side downward in a vat or chamber, likewise constructed of some non-conducting material; into this chamber the electrolyte is placed. A perforated carbon anode is hung inside of the bell and the chlorine generated at this anode is carried away by an exit-tube which passes through the upper part of the bell. The cathode is placed in the outer vessel and the alkaline lye which is generated at the

cathode passes off through an overflow placed at the top of the vat.

Generally a number of such bells are linked together in parallel; the total number of bells employed in a plant, in some works, runs up to twenty or thirty thousand. Details as to the current density and other working conditions are not publicly known, but Foerster* infers that the ND_{100} ranges from 2 to 4 amperes, that the temperature does not exceed 30° or 35° C., and that the voltage used is about 4 or 5 volts.

III. **The Mercury Process.** — The essential feature of the processes using mercury as the cathode is the formation of an amalgam of the alkali metal liberated by electrolysis.

In Castner's process — the Castner Electrolytic Alkali Company was the first to manufacture chlorine and caustic soda — the production and the decomposition of this amalgam are carried out in the same apparatus. A box is divided into three compartments by the use of partitions which reach almost, but not quite, to the base of the box; this base is covered with a layer of mercury. The two outside compartments are closed on top and suspended in them are the carbon anodes which reach down almost to the mercury.

The electrolyte employed is a solution of sodium chloride, which suffers electrolysis in the outer chambers. The central chamber, which contains an iron electrode in a weakly alkaline solution, serves for the decomposition of the amalgam into mercury and sodium-hydrate. The whole apparatus is so arranged that it can be given a rocking motion and during the operation it is kept constantly moving.

The electric current is obliged to pass from the anodes by way of the mercury to the cathode which is situated, as will be recalled, in the central compartment. The mercury, acting as cathode in the two outer chambers, amalgamates with the sodium and then gives up this alkali in the cathode chamber, where the mercury acts as anode, the alkali dissolv-

* *Liber. cit.* p. 417.

ing in the water and the hydrogen gas escaping. The ND_{100} at the cathodic mercury is about 7 amperes, at the anodic mercury, about 12 amperes; the voltage is about 4 volts. The product obtained by the Castner process is very pure. The chlorine is generally turned into chloride of lime.

A process differing from but planned on lines similar to those just referred to, is Kellner's process, and in England the Castner-Kellner Company makes use of a method embodying the fundamental principles of both of these systems.

A. II. INDIRECT ACTION PROCESSES.

Electrodeposition from Fused Electrolytes.

Introduction. — In electrolytic processes where the product is obtained from a fused electrolyte, the electrical energy is in part used for the actual electrolytic work and in part for the fusing of the electrolyte.

The relation between electrical energy and heat energy is expressed by Joule's law (1841): "the heat developed in a conductor is proportional to the resistance encountered and to the square of the strength of the current."

If: resistance $= R$
current strength $= C$
heat $= H$

then, $H = C^2 R\ 0.24$.

The heat thus generated electrically, not chemically, is termed Joule's heat.

To illustrate, assume:

Resistance equal to 2 ohms.

Current strength equal to 50 amperes.

Then, $50 \times 50 \times 2 \times 1 = 5000$ joules per second.

As one joule equals 0.00024 large Calorie, or 0.24 small calorie, 5000 joules $= 5000 \times 0.00024 = 1.200$ Calories or, $5000 \times 0.24 = 1200$ calories.

In passing through a circuit embracing an electrolyte, Joule's heat is generated in all parts of the circuit in amounts proportionate to the resistance of the respective parts of the circuit and to the square of the current.

The actual temperature to which an electrolyte thus attains in a given time under given conditions of current strength and resistance depends upon its mass, its specific heat, and upon the success with which loss of heat by radiation, and by other causes, can be avoided.

An important point to be borne in mind in attempting to secure a metal from a fused electrolyte is that the boiling point of the metal must not lie too close to the point of fusion of the electrolyte, otherwise volatilization of the metal would almost keep pace with its electrolytic production.

The metals whose production from a state of fusion shall now be briefly considered are aluminium, magnesium, and sodium.

Aluminium. — Various processes have been devised for the electrolytic winning of aluminium. The methods, however, principally employed are the Héroult process and the Hall process. Chemically, these two processes are very much alike, in both, pure alumina (Al_2O_3) is added to the fused double fluoride of aluminium and sodium, Al_2F_6, 6 NaF, a mineral called cryolite.

In putting the process into operation the cryolite is first brought into a state of fusion in iron furnaces and then the anodes are lowered into it and electrolysis commences. As the aluminium separates at the cathode, alumina is fed into the bath so as to keep the amount of aluminium present in the electrolyte about constant. The metal being specifically heavier than the fused electrolyte, sinks to the bottom of the fusion chamber, whence it is tapped, generally once a day. The anodes are made of carbon, the cathodes are generally made of iron, but these also can be made of carbon.

In the Hall process, the amperage used per fusion chamber

is about 10,000 amperes, the voltage employed, about 5 volts. The temperature of the bath is held in the neighborhood of 1000° C., being kept as low as possible. The fusion chambers are discharged at stated intervals.

In the Héroult process, about 8000 amperes per furnace are required, the voltage ranges from 3 to 5 volts, the $ND_{100} = 190$ amperes and the temperature is held between 750° and 850° C.

The chemical reactions taking place during electrolysis consist in the liberation of aluminium at the cathode and of oxygen at the anode; this oxygen of course combines with the carbon anodes to form carbon monoxide. The pure alumina which is used in the process is generally obtained from the mineral bauxite, which is passed through a preliminary purifying operation by roasting and by subsequent treatment with caustic soda, or, according to a recent process devised by C. M. Hall, bauxite as well as other impure aluminium oxides are purified by fusion with the electric current, the impurities present being reduced in the fused bath.

Estimates vary as to the amount of electrical energy necessary in the Hall process, for the production of one kilogram of aluminium. Bucherer places it at 32.7, Becker at 30, and J. W. Richards at 22 kilowatt-hours.

Of the total electrical energy consumed in the production of aluminium, it is calculated that about four-fifths are used for the heating and the balance for the actual electrolytic work. The electrical energy, which is expended in effecting the separation of metallic aluminium from its chemical combinations, can of course be recovered as heat energy when the metal is caused to re-combine with oxygen; this is the case, for instance, in the Thermite process.

According to the report of the United States Geological Survey, the world's production of aluminium in 1903 was over eighteen million pounds, of which seven and a half millions were produced in the United States, the balance being made in Switzerland, France, and Great Britain.

In 1904 production of this metal in the United States, which in 1883 had amounted to only 83 pounds, was 8,600,000 pounds. The sole producer in the United States is the Pittsburg Reduction Company, which at present has five plants in operation.

The purity of commercial aluminium is about 99%, the impurities constituting the balance are principally iron, copper, silicon, and carbon.

Magnesium. — The raw material from which magnesium is won electrolytically is carnallite, a double chloride of potassium and magnesium, which is carefully dehydrated before fusion; its fusion temperature is be ow 700° C.

As in this process the product liberated at the anode is chlorine, the apparatus must of course be arranged so as to prevent this gas from combining with the magnesium which is set free at the cathode. In one form of apparatus this is accomplished by conducting the electrolysis in a steel vat, the walls of which serve as cathodes; in the center of this vat there is introduced the carbon anode, inclosed in a porcelain cylinder, which is provided with a tube from which the chlorine gas escapes.

The ND_{100} used is from 11 to 15 amperes, the voltage is about 4 volts. Care is taken to have the electrodeposition of the magnesium take place in an inert atmosphere; for this purpose either nitrogen, or some gaseous mixture devoid of free oxygen, is introduced into the cathode compartment.

Sodium. — The most important process for making sodium electrolytically from caustic soda is Castner's process. The products of the electrolysis are sodium, hydrogen, and oxygen. The anodes are made of nickel, of iron, or of steel, and are annular or cylindrical in shape.

The cathode, generally made of nickel, projects upward into a collecting chamber and into a cylinder of wire gauze in which the metallic sodium accumulates, and which hinders it from passing into the anode-chamber; the hydrogen gas in

the cathode chamber prevents the oxidation of the sodium. The temperature is carefully held between 310° and 330° C. The voltage used is about 5 volts, and each furnace uses about 1200 amperes.

A recent process, devised by E. A. Ashcroft, consists of a cell wherein fused sodium chloride, the electrolyte, rests on fused lead, which acts as cathode; the anode is made of carbon and the chlorine is there liberated. The sodium alloys with the fused lead, and this alloy is conveyed to an outside compartment where it acts as the anode, the cathodes being either iron or nickel, and the electrolyte consisting of fused sodium hydrate. In this outer chamber metallic sodium is set free at the cathode.

A process devised by Acker Bros., makes use of fused sodium chloride as the electrolyte, the same being well dried before fusion. The anodes consist of graphite, and fused lead serves as cathode, as in the Ashcroft process.

The lead-sodium alloy is decomposed at red heat by steam blown in under pressure, the resultant products are molten lead, sodium hydrate, and hydrogen gas. The voltage employed is about 7 volts, the ND_{100} about 290 amperes, each furnace taking 8000 amperes; a part of this energy is used to keep the sodium chloride in a state of fusion without application of heat from any outside source. The chlorine evolved was formerly turned exclusively into chloride of lime, but recently the Acker Process Company have devised new uses for the chlorine, and among other products now manufacture tetrachloride of carbon and tetrachloride of tin.

Electrothermic Processes.

Electro-furnaces. — In conductors of the first class, that is to say, in all metals and in carbon, *all* electrical energy can be converted into heat energy.

The formula by means of which the heat equivalent, in calories, of a given amount of electrical energy can be figured

is, it will be recalled, very simple. Designating the heat equivalent by H, the resistance by R, the current strength by C, the result desired, expressed in gram calories, is:

$$H = C^2R\,0.24$$

Probably the first one to suggest the application of electrical energy for electrothermic work on a commercial scale, was Sir William Siemens, in 1880.

The transformation of electrical energy into heat energy is, in practice, accomplished in several ways, and at least four types of electrical furnaces may be distinguished:

1. The arc furnace.
2. The resistance, or incandescent furnace.
3. The transformer, or induction furnace.
4. The tube furnace.

Arc furnaces may be divided into two groups, direct and indirect arc furnaces. In the former, the material to be subjected to the influence of the heat generated by the transformation of electrical energy, is exposed directly to the electric arc; in the indirect type the material to be treated is not exposed to the direct action of the arc but receives its heat indirectly, the heat being reflected from the interior of the chamber in which the reaction takes place and into which the electrodes project.

Of course the forms which may be given to arc furnaces are varied, but the principal feature embodied in all furnaces of this description is a hearth constructed of some fire-resisting material, fire-brick or the like, and carbon electrodes, which project into this fusion chamber. The current is supplied by means of heavy cables clamped to these carbon electrodes.

As before stated, the material to be acted on may be either exposed to the direct heat of the arc, or else it may be so placed that it receives only radiated and reflected heat from

the walls and the roof of the furnace chamber. An illustration of the former type is offered by the aluminium furnace during the time when the cryolite and the alumina are being fused, that is to say, before electrolysis proper has begun. As an illustration of the indirect action type of arc furnace, there may be mentioned the furnace used by Moissan in some of his famous researches, and the De Chalmont furnace employed for the reduction of metallic silicides, for in these the charge is also exposed only to the radiated heat of the arc.

Resistance, or incandescent furnaces, were probably first devised by E. H. Cowles and A. H. Cowles, of Cleveland, Ohio, in 1885. The principle upon which these furnaces are constructed is to have some material in the circuit of the electric current which will offer a high resistance to the passage of the current, in consequence of which high temperatures are generated.

Where highest temperatures are sought, the arc furnace is indicated, but where closer regulation and control of the working temperatures are demanded, resistance furnaces offer decided advantages.

The degree of temperature attained in the resistance furnace is determined by the magnitude of the current, the time during which this flows, and the amount of resistance offered by the circuit through which the current passes.

The ultimate temperature attained is the outcome of the rate at which heat is generated in the resistant body — the core, and the rate at which this heat suffers dissipation. The point at which these two conditions counterbalance each other determines the highest temperature of the furnace.

In the resistance furnace, the material to be heated can itself be made the resistant body, or the latter can be embodied as a core in the material to be treated. In such cases, the material generally employed is carbon, coarsely grained.

The Acheson furnaces well illustrate that type of the

resistance furnace in which the core is, in part, formed by the material to be acted upon.

Borcher's furnace is an instance of the other type of resistance furnace, that is to say, of a furnace in which the resistance core is independent of the charge. A thin pencil of carbon is imbedded in the mass to be subjected to heating, and a powerful electric current is transmitted to this carbon pencil by carbon bars or cylinders very much greater in diameter than the pencil. Naturally an intense heat is generated at the pencil owing to the resistance offered, and as carbon does not volatilize appreciably below 3000° C., very high temperatures can conveniently be obtained.

In transformer, or induction furnaces, of which Kjellin's furnace for steel production may serve as a type, the heat is produced by induction, the current in the furnace being induced by an alternating current passing through an outside conductor near by, generally a coil of many turns which incloses the furnace.

Induction furnaces are advantageously used for smelting platinum; in Sweden they are used for working iron ores and, as indicated above, for the production of a special grade of steel.

The characteristic feature of tube-furnaces is the tubular form of the hearth, the current passing through and heating the walls of the tube, which is constructed of some refractory material.

H. Noël Potter has devised a number of furnaces of this type in which he has sought to secure a uniform heating of the whole tube, satisfactory terminal connections, and a ready replacement of the worn parts. One of the forms he has devised consists of a carbon tube supported by carbon rings between which magnesia, covered by asbestos, is packed, the whole being inclosed in a porcelain tube.

Another of Potter's furnaces consists of a tube made from the oxides of magnesia, yttria, and zirconia inclosed in a

second tube made of one of these oxides. On this outer tube, over a layer of mica, a coil is wound in which electrical action is started; the actual heating effect, however, is produced in the interior tube. This furnace is chiefly used for the baking of Nernst lamp glowers.

Among other tube furnaces, mention should be made of the one designed by A. H. Eddy, used for the application of enamels, and that of Nernst and Glaser, which has a resistance-tube made of electrolytic oxides, the outer tube consisting of loosely packed oxides and all inclosed in a jacket designed to prevent loss of heat by radiation.

A very convenient electro-furnace for certain laboratory purposes is used by the Technische Reichsanstalt at Charlottenburg, for high temperature work. It is made of several concentric porcelain tubes, and the heating is effected by passing an electric current through wires which are wound upon some of these tubes.

Recently an electric furnace which can be used in connection with a vacuum, and for general analytical purposes, has been devised by the firm of Heraeus, Germany.* These furnaces can be used with direct current at a potential of from 65 to 220 volts, and require only from 1.5 to 2.5 amperes. The uniformity of temperature, which can be maintained in these furnaces, and the avoidance of reducing gases, which the use of fuel gas often entails, are valuable features.

In some electrothermic furnaces the process is a continuous one, that is to say, the process is not interrupted for the introduction of charges, nor for the withdrawal of the product. It is, however, not always possible to arrange a working system in this way, and therefore many furnaces are intermittent in their action.

The electric furnace undoubtedly permits the securing of a higher temperature than can be secured through any other device. Whereas the maximum temperature obtainable by

* *Chemiker Zeitung*, 1905, Vol. 29, p. 1209.

the combustion of fuel under the most favorable conditions is probably not above 2000° C., the temperature of the electric arc has been estimated — by Violle in 1893 — at about 3600° C., and it will probably be reasonable to regard this as the highest temperature maintainable in arc furnaces under ordinary conditions. In furnaces provided with additional protection against loss of heat by radiation, for instance, in furnaces having an additional lining of some good non-conductor, like magnesia or chalk, temperatures up to 4000° C. can be secured; speaking, however, of practical electrical furnaces working on a commercial scale, the working temperatures of these will range from about 2000 to 3500° C.

Where no electrochemical, but only electrothermic work has to be done, preference is given to the alternating rather than to the direct current.

In considering the cost of electric furnaces, the cost of the electrical energy to be used is naturally a factor of the greatest importance. Where such energy has to be generated by the combustion of fuel, the cost will necessarily be high, because only a small percentage, possibly from 5 to 8% of the heating power of the coal which is burned under the boiler, is actually gained in the form of electrical energy. Where water-power is available, the conditions are far more favorable, and it does not appear improbable that in the near future wind-power may be made to serve for the cheap generation of electricity for electrothermic, as it now does for other purposes.*

Electro-Furnace Products. — A number of substances have been prepared by the aid of the high temperatures made available through electro-furnaces. Some of these are metals won in the free state through the dissociation of their compounds — for carbon at the heat of the electro-furnace can

* Paul la Cour (Aus dem Dänischen übersezt von J. Kaufmann): Die Windkraft und ihre Anwendung zum Antrieb von Elektrizitäts-Werken, Leipzig, 1905.

remove oxygen from any metallic oxide known; other substances produced are compounds, the chemical union of their constituents being effected by the aid of electrical energy.

The metallic products of electro-furnaces shall be first considered.

Chromium. — This metal has been obtained in the electric furnace from various raw materials. If a mixture of chromic oxide (Cr_2O_3) and carbon are fused, carbides of chromium result, and from these, by fusion with lime, the greater portion of carbon can be removed. The metal thus produced contains between 97% and 98% of chromium, and carbon, iron, and silicon as impurities. If perfectly pure chromium is required, this can be secured by fusing together chromic oxide, chromic carbide, and lime.

In the Aschermann process, a mixture of chromic oxide and antimony sulphide are fused together in a graphite crucible, and from the resultant alloy of chromium and antimony the latter element is removed by heating.

Iron and Steel. — Under existing economic conditions it is evident that electro-smelting of iron ores and the electro-production of steel is practically feasible only where pure ores may be worked and where electric power can be cheaply produced.

There is no question but that an ore so treated and a steel so produced may be of superior quality, at least when produced in certain types of electro-furnaces, for in some types of furnace the influence of impurities can be avoided to a great extent.

A number of electric furnaces have been designed for the purpose of working iron ores and of producing steel.

Paul Héroult, of France, was, in 1900, the first to make steel electrically on a commercial scale. He devised several kinds of electro-furnaces for ore smelting and for steel refining. One of these somewhat resembles a Bessemer converter in its

construction, but contains two vertical carbon electrodes between which and the conducting charge two arcs are struck in series. An exceedingly fine tool steel can be produced in this furnace from steel scrap and cast iron. An alternating current of 60 volts and 4000 amperes is used in the process.

At present works are in process of erection at Syracuse, N.Y., by the Holcomb Steel Company, where the refining of steel will be done by the Héroult method. Further experimental work with the Héroult process for the electro-smelting of ores and the manufacture of steel will shortly be under way at Sault Ste. Marie.* As Canada is rich in high-grade iron ores and commands vast water-power, the prospects there for a successful outcome of an electro-process of this kind are certainly promising.

The Gin furnace consists of a zigzag-shaped trough, in which the premolten cast iron which is to experience treatment acts as resistance and transforms the electric energy into heat. The terminals are hollow steel blocks cooled by circulation of water. The iron is changed to steel either by the addition of oxide of iron, or else by the introduction of scrap iron.

In the Keller furnace the charge is fed in from the top, as in a blast furnace. The electrodes, four or more in number, are inserted vertically and are independent of one another; fusion begins near the hearth and extends upwards, the gases formed preheating the ores. From the smelting furnace the reduced iron flows into the steel fining furnace in which two vertical electrodes are used. The voltage of the reducing furnace is about 30 volts, of the steel furnace about 70 volts; in France about 2800 kilowatt-hours are required for making one ton of steel from ordinary ores.

In the resistance furnace devised by Dr. Borchers, the car-

* *Electrical Review*, 1905, Vol. 47, p. 672.

bon to be used is placed between the electrodes as resistance, and the ore to be treated is packed around this core.

F. C. Weber has devised an arc smelting furnace in which the descending charge passes through a series of arcs, each one of which can be independently controlled; this permits of an accurate regulation of temperature in the various zones of the furnace.

Among other processes devised for iron and steel work mention should be made of the process of M. Ruthenberg, especially adapted to the working of metalliferous sands and of finely divided ores at a relatively small expenditure of energy, and of the process of Kjellin, in Sweden, which, as previously mentioned, is said to produce a steel of excellent quality. Kjellin's furnace is of the induction type; a current of 3000 volts is supplied and the current passing through the charge is about 30,000 amperes. By avoiding the use of electrodes the steel is not open to the absorption of impurities and hence the high grade product. The cost is reported to be comparatively low.

Manganese. — A crude metal containing about 90% of manganese is obtained by fusing the oxide of manganese in an arc furnace. As manganese is rather a volatile metal the temperature conditions require to be carefully regulated, for the heat must not be allowed to become too great.

An iron manganese alloy (ferro-manganese) is prepared by the Simon process in France, by fusing together an oxide of manganese and fluorspar. Part of the electric energy used is expended in electrolytic action, possibly about 25% of the total being used for this purpose, while the balance produces the necessary heating effect. The ferro-manganese alloy resulting from this process contains about 85% of manganese and from 7 to 8% each of iron and of carbon.

Molybdenum. — Heating molybdenum sulphide with carbon produces a crude molybdenum which contains approximately 10% of impurities, of which carbon and iron are the

most important. This crude metal when mixed with molybdenum oxide and subjected to fusion in an arc furnace parts with its carbon and is won in a pure condition.

Titanium. — The fusing point of titanium is higher than that of any metal thus far obtained by thermo-electric work. Moissan did not succeed in completely fusing a small amount, possibly 350 grams, of a mixture of titanic acid and carbon even by the expenditure of 2200 amperes and 60 volts. The metal titanium combines readily with nitrogen, but this compound, the nitride, can be broken up by raising the temperature of the arc sufficiently high; in so doing, however, some of the carbon of the arc is apt to enter into chemical combination with the titanium, this resulting in the formation of a carbide of titanium from which it is most difficult, if not impossible, to obtain a pure metal.

Uranium. — This metal can be obtained in a pure state from its oxide by heating the latter with carbon. Uranium is volatile in the electric arc, and at a temperature of 1000° C. readily enters into chemical combination with nitrogen.

Vanadium. — Vanadium can be obtained by the Gin process* from the fluoride of vanadium. The anodes used are rods especially prepared from vanadium trioxide, retort carbon, and rosin, shaped under hydraulic pressure and baked at very high temperatures. The cathode is made of iron. The anode ND_{100} is approximately 200 amperes, the cathode ND_{100} about 600 amperes, the voltage about 12 volts.

Alloys with iron, the so-called ferro-vanadium alloys, are also prepared by this process.

Tungsten. — Moissan succeeded in preparing this metal by fusing together tungstic acid and pure carbon. It is important that an excess of carbon be avoided and that the temper-

* *Bericht des V. Int. Kongresses für Angew: Chemie*, Berlin, 1903, Vol. 4, p. 744.

ature be kept sufficiently low so that the metal may not fuse completely, for if it does, some of the carbon will enter into chemical combination with it, forming carbide of tungsten.

* * *

Electro-furnaces are also used for the manufacture of other substances — not metals — which, before the coming of the electro-furnace were either unknown, or were made by other processes. Of these products the following should be mentioned.

Alundum, or artificial corundum, is an abrasive, crystalline in form, and extremely hard and sharp in grain, prepared in the electric arc furnace from calcined bauxite or from gibbsite, by the Jacobs process.

Barium-Hydrate. — In a process also devised by C. B. Jacobs, barium sulphate (Barytes) is treated in an electric furnace in the presence of carbon. The ore is first reduced to barium sulphide and this, reacting with additional barium sulphate, forms barium oxide and sulphur dioxide gas. The barium oxide is dissolved in water, and the hydrate thus formed is obtained as crystallized barium hydrate of high grade purity.

Carbides. — A class of bodies termed the carbides is formed in the electric furnace by reducing the oxides of some metals and non-metals in the presence of an excess of carbon. Either arc or resistance furnaces may be used for the purpose; often both systems come into play in one operation through the unavoidable arcing which occurs in the working of some resistance furnaces.

While the list of carbides embraces possibly some twenty odd compounds only a very few of these have any appreciable commercial importance, calcium-carbide is probably the most important of them all.

Calcium-carbide. — In 1892 Moissan announced that he had made calcium-carbide, a compound of calcium and car-

bon, by means of the electric furnace. Towards the end of the same year, T. L. Willson stated that he had, by fusing lime and carbon together electrically, obtained a body yielding acetylene when brought into contact with water. This investigator, it appears, had made calcium-carbide as early as 1888, at Spray, North Carolina, but did publish the data at the time.

The formation of calcium-carbide is shown by the formula:

$$CaO + 3\,C = CaC_2 + CO$$

When the current density through the resistance core attains to 1.2 amperes per square mm., the formation of the compound begins and at a current density of 2 amperes per square mm., complete fusion is attained at the core; the rest of the charge, further removed from the core, assumes a pasty condition, the temperature of the core experiences a gradual lowering, and, in consequence, calcium-carbide, the resultant product, is intermingled with other substances.

Practically, the formation of calcium-carbide does not occur below a temperature of 2000° C. and probably a temperature higher than this is the true temperature of the reaction, which, as previously indicated, is partly an arc and partly a resistance reaction.

A slight excess of carbon should always be provided, for otherwise calcium and carbon monoxide are apt to be formed through the interaction of the lime and the carbon and the carbide would in consequence be exposed to contamination. In fact, it is important to aim at the production of a pure calcium-carbide from the outset, because this carbide when once formed is practically neither fusible nor soluble, and therefore offers great, if not insurmountable, difficulties to any subsequent purification.

To obtain as pure a calcium-carbide as possible the addition, before fusion, of manganese peroxide and of calcium

carbonate to the original charge of lime and carbon has been advocated; this process is known as the Hewes process. In another process, devised by Rathenau, iron, or oxide of iron, is added to the charge before fusion so that the iron may combine with and remove all of the silicon present as ferro-silicon.

In the manufacture of calcium-carbide, either the direct or the alternating current may be used; for some reasons the latter is preferable.

The commercial value of a given calcium-carbide depends, of course, upon the amount of acetylene gas (C_2H_2) which it will yield on reacting with water. The equation reads:

$$CaC_2 + 2\,H_2O = C_2H_2 + Ca\,(OH)_2$$

The theoretical yield of one kilogram of pure calcium-carbide is about 350 liters of acetylene gas, at normal temperature and pressure; from the commercial product, however, generally not more than 85% of this yield are obtained.

Carbon bi-sulphide. — E. R. Taylor, at Penn Yan, New York, produces carbon bi-sulphide in electric furnaces. These measure about 41 feet in height and 16 feet in diameter, the diameter decreasing towards the top. These furnaces are constructed of a steel shell and are lined with refractory fire brick or some similar substance.

The electrodes, four in number, are placed 90° apart and are re-enforced in the interior of the furnace by a continuous supply of coke or broken carbons, which are fed into the furnace by conduits.

The sulphur is placed at the bottom of the working chamber of the furnace and extends up to and around the electrodes. Annular chambers situated in the lower part of the furnace are kept supplied with sulphur, which is fed in at the top and which runs down into the furnace in a molten condition.

The vapors of sulphur passing through the charcoal,— which fills the body of the furnace, combine with it and form

vapor of carbon bi-sulphide; this passes off through a tube near the top of the furnace into a condenser, wherein the vapor becomes liquefied. A subsequent distillation insures a product almost entirely pure.

The furnaces are arranged with a view to economize most of the heat generated in the process and are continuous in their action. The output is about 4500 kilograms of carbon bi-sulphide in 24 hours. The working power is furnished by turbine water-wheels, although a steam engine is held in reserve in case, for any reason, the water power should fail.

Glass. — Glass when in a fused condition is an electrolyte, and a number of electrothermic processes have been devised for its manufacture. In some of these processes as in the Shade process, an arc furnace is employed, in which between four and six kilowatt-hours are required to produce one kilogram of molten glass.

In other processes, for instance, in that of Reich, a resistance furnace is used. In a recently designed furnace of the resistance type, kryptol — which is essentially pure carbon of uniform grain, is utilized as the heating material.* The kryptol is packed around the vessel holding the charge of glass and by this arrangement the loss of heat by radiation is materially reduced. Carbon electrodes are employed, the current used is about 100 volts, and the operation is carried on at a temperature materially below that of an arc furnace.

In still other furnaces for the manufacture of glass, a combination of the arc and the resistance principle is employed; an illustration of this type is the August Voelker furnace, which is used in Germany and which is reported to be very effective in its working.

Graphite. — Artificial graphite † is another product made by the Acheson Company at Niagara Falls. It is prepared in

* *Electrical Review*, 1905, Vol. 47, p. 445.

† Consult C. P. Townsend, *Electric World*, 1901, for an historical resumé of studies on artificial graphite.

a resistance furnace from anthracite coal or from coke. The charge is separate from the core, which consists of carbon rods extending through the charge. At the beginning of the operation these carbon rods transmit the whole of the current and, in consequence, become highly heated. The high temperature thus generated, converts that portion of the charge immediately adjacent to the core into graphite; this graphite then conducts a part of the current and thus gradually the zone of reaction extends farther and farther through the mass.

The Acheson Company also graphitize electrodes, these in the process being exposed to a temperature above the temperature of volatilization of silicon, iron, and aluminium.

Nitrogen Fixation. — Chemical combination of atmospheric nitrogen and oxygen, and the union of the resultant nitrogen-oxides with water to form nitric acid, has been achieved by F. C. Crocker, C. S. Bradley, and D. R. Lovejoy.

The works are situated at Niagara Falls. Dry air is passed through a chamber provided with stationary negative electrodes which are placed in vertical rows and before which there revolves a central shaft carrying the positive electrodes ending in fine platinum wires. The negative terminals are in connection with choke-coils which are kept submerged in oil. A current of 10,000 volts is employed, and about 69,000 arcs per minute are flashed through the air which passes between the electrodes. The treated air contains between two and three per cent of nitrogen oxides. Seven HP. hours are said to produce about one-half kilogram of nitric acid; this acid and calcium nitrate — valued as a fertilizer, are among the products manufactured at the Niagara Falls plant.*

Oxone.— Oxone, a fused peroxide of sodium, is manufactured

* For a recent comprehensive review of the work done on atmospheric nitrogen see:

A. Neuburger, *Die Verwerthung des Luftstickstoffs, Zeitschrift für Angewandte Chemie*, 1905, pp. 1761, 1810, 1843.

by the Niagara Electrochemical Company.* It is a stony compound which yields oxygen gas when brought into contact with water. It is employed for therapeutical purposes and its use for the sterilization of foods has also been recommended. Analogous peroxides exist of calcium, magnesium, and zinc.

Phosphorus. — Various furnaces have been devised for the electro-winning of phosphorus and a large proportion of the world's supply of this article is now obtained by electrothermic methods.

In the Readman and Parker process, mineral phosphate, finely ground, is mixed with sand and carbon and introduced into a furnace from which all air is carefully excluded. This furnace is of the resistance type; the electrodes are made of carbon and enter the lower part of the furnace, the hearth. The phosphorus is caught under water as it distils from the furnace.

In the Machalske process an arc furnace is used and an alternating current is employed. Tri-calcium-phosphate, silica, and carbon are the crude materials used, phosphorus, carbon-monoxide, and a slag of calcium silicate are produced.

Silicides. — The silicides are a class of compounds similar in type to the carbides, but with silicon in the place of carbon.

The silicides of calcium, barium, and strontium, expressed respectively by the formula: $CaSi_2$, $BaSi_2$, $SrSi_2$, were discovered by C. B. Jacobs and are all manufactured by The Ampere Electrochemical Company.†

To prepare these compounds the silicates of the above-mentioned alkaline earth metals are reduced in the electric furnace in the presence of sufficient carbon, or, a mixture may be made of carbon and silica, together with some of the salts

* F. A. J. FitzGerald, *Electrochemical and Metallurgical Industry*, Vol. 3, 1905, p. 253.

† Jacobs, *American Institute of Electrical Engineers*, 1902.

of the metals mentioned and the mixture fused in the electric furnace.

These silicides are crystalline in structure; when brought into contact with water they decompose it, and yield a silico-hydrate of the metal and free hydrogen gas. Of the silicides mentioned a given weight of calcium silicide furnishes the greatest volume of hydrogen gas, a corresponding amount of barium silicide will yield only about one-half as much. Commercially, these compounds are used in the preparation of hydrogen gas, and they are also employed as powerful reducing agents.

Copper silicide (CuSi) is another member of this group; it is principally used as a reducing agent in the preparation of a certain class of copper alloys, the so-called silicon bronzes. Copper silicide contains about 30% of silicon.

Ferro-silicon can be made from the slags of steel furnaces. Two ferro-silicon alloys, the one containing about 30% and the other about 50% of silicon and approximately 5% of carbon, are used in the manufacture of steel, especially of armor plate. Ferro-silicon is far more effective than carbon as it evolves 7800 calories, where a corresponding amount of carbon yields approximately but 2500 calories.

Silicon Carbide. — Technically known as carborundum, silicon carbide (SiC) is produced by the fusing of sand and carbon, as expressed by the equation:

$$SiO_2 + 3\,C = SiC + 2\,CO$$

Acheson first made carborundum in 1893. The operation is conducted in a furnace built up of loose brick, and each furnace serves for one run only. An alternating current is conveyed by leads to bronze end-plates to which the carbon electrodes, bundles of carbon rods, are attached; between these electrodes the core of coarsely powdered coke is laid. The charge, consisting of sand, coke, sawdust, and a little salt, is placed about this core. Each furnace takes about

1000 HP. The initial voltage is about 200 volts, but this drops by fully 60% as the heating of the core progresses. The total process takes from twenty-four to twenty-six hours, that is to say, the electric current is passed for that length of time, then the furnace is allowed to cool and is dismantled.

Various products are formed, segregated in layers. The central core is graphite, next to this a layer of crystallized carborundum, and then a layer of greenish silicon carbide, amorphous in structure, generally intermingled with some of the original charge which has not been transformed. This substance, essentially a compound of carbon and silicon, is termed white stuff; all of the material beyond the white stuff is reincorporated with the next charge. The manufacture of white stuff has been made the subject of a separate patent by Acheson.

Carborundum consists practically of 70% of silicon and 30% of carbon; it is apt to hold as impurities some iron, aluminium, and calcium.

About 8.6 kilowatt-hours are required to produce one kilogram of carborundum and the temperature must be carefully regulated to guard against volatilization of the silicon; 3800° C. is approximately the temperature of formation of carborundum.* This substance is used largely as an abrasive, for furnace linings, and for purposes of deoxidation in the manufacture of steel.

Siloxicon. — This substance, originally obtained as a by-product in the production of carborundum is now a separate article of manufacture. It is a chemical compound of the elements carbon, silicon, and oxygen, and its constitution is expressed by the formula, Si_2C_2O.

It is made at a temperature of about 2700° C., in furnaces similar in construction to those used in the manufacture of

* J. Wright, *Liber cit.* p. 42. Confer; F. A. J. FitzGerald, *Electrochemical and Metallurgical Industry*, 1906, p. 53.

carborundum. Siloxicon is very refractory at high temperatures and is soluble only in hydrofluoric acid; as it is self-binding it needs only to be moistened with water and can then be molded into any shape desired, preliminary to firing. It is used for the manufacture of fire-bricks, crucibles, etc.

ELECTRO-ORGANIC PROCESSES.

B. I. **Direct Action Processes.** — Electro-reactions in the domain of organic chemistry, may also be divided into direct action and into indirect action processes. The former group would include all actions in which electrical energy is directly applied, for instance, all electrolytic processes — whether these be processes of substitution, oxidation, or reduction; it would also embrace reactions effected by silent discharge. The other group would include all indirect effects such as thermo-electric and photo-electric processes.

Speaking of the first of these groups, attention has been given chiefly to processes of reduction for the reason that these can be most conveniently studied with reference to certain groups in the molecule, whereas processes of oxidation are, as a rule, apt to involve the molecule as a whole in chemical change.

Reference cannot here be made in detail to the many interesting and valuable results obtained in organic chemistry by processes of electro-analysis and electro-synthesis, which afford the great advantage of permitting the bringing about of chemical reactions without necessitating the introduction of any chemical reagents. It must suffice to remark that within the past decade great advances have been made in the application of electrical energy to the solving of numerous problems in organic chemistry and that the field is still a very promising one for the investigator.*

* Consult C. W. Loeb, *Die Elektrochemie der Organischen Verbindungen*, 1905.

Among electro-technological operations, dealing with the manufacture of organic substances, there should be cited the preparation of fine chemicals and of dye-stuffs; among the chemicals thus made there may be mentioned, vanillin (from iso-eugenol), iodoform, chloroform, and bromoform; among the dye-stuffs so prepared, aniline, alizarin-black and fast yellow dyes.

Experiments looking to the application of electrical energy to agricultural problems were tried many years ago, and a number of attempts have been made to foster the growth and the yield of crops by stimulating the soil by electricity.

Thus Spechnew, in 1889, exposed seeds, after they had been immersed in water, to the action of induction currents and secured their germination in from two to eight days, while control-seeds which had not been treated with electricity, required from four to fifteen days before they germinated. These results were confirmed by other investigators, and several cases are on record where it was found that both the yield and the growth of flowers and vegetables were remarkably improved and stimulated by passing electric currents between large copper electrodes buried in the soil. Interesting results along such lines were, among others, obtained by the Hatch Experimental Station in Amherst, Mass., as early as 1892.

B. II. **Silent Discharge Processes.**— In the silent electric discharge, electrical energy is continuously passing from one conductor to another through an intervening space which is filled with a gas or with a mixture of gases.

The apparatus employed for silent discharge work can be, and is, constructed in various forms, but the essential feature of construction in all of them is an arrangement which obliges the electric discharge to pass through a layer of the gas acted upon.

Frequently the current is passed between two layers of sulphuric acid contained in very thin glass vessels, the elec-

trical energy being obliged to pass through the containing glass walls and through the gas confined between them. In other forms of apparatus a metallic foil — tin-foil, aluminium-foil or silver, is used instead of the acid conductors. The simplest form of apparatus used for the purpose consists of two metal plates between which the gas to be acted upon is placed; as these metal plates are, however, apt to become worn and roughened by the discharges, there is always some danger of spark discharges. Aluminium is possibly the metal best suited for constructions of this description.

In every case the thinner the layer of gas through which the electric discharge must pass, the more effective is the reaction. In rarefied gases the discharge is often accompanied by luminous phenomena, the so-called Geissler tube effects.

As there is no appreciable elevation of temperature in these reactions, endothermic compounds may be formed under the influence of the silent discharge, and for this reason these phenomena and reactions are of the greatest value in bringing about simple organic syntheses, similar to those which plants effect under the influence of sunlight.

Berthelot, experimenting with the silent discharge, showed that atmospheric nitrogen could be bound in the form of complex organic compounds, which, when treated with soda-lime at high temperatures yielded ammonia. The results he obtained are of special interest, as they point to the possibility of the assimilation of atmospheric nitrogen by plants under the influence of atmospheric electricity.

Thus Berthelot * pointed out, that in clear weather there is a difference of potential of from 20 to 30 volts between two layers of air which are but one meter apart, and in rain storms this difference of potential may rise to about 500 volts. As Berthelot achieved a fixation of nitrogen by carbohydrates by means of a difference of potential of 8 volts only,

* *Compt. rend.* 1900, Vol. 131, p. 772.

his suggestion, that in nature the silent discharge is an active agent in plant-life and growth is certainly most plausible.

A number of synthetic reactions have been achieved in the laboratory by means of the silent discharge. Thus, under its influence, carbon monoxide and nitrogen have been made to yield formaldehyde and marsh-gas (Brodie, 1872), and, it is interesting to recall that formaldehyde was used by Butlerow more than forty years ago in the synthesis of sugars.

Collie* found that carbon dioxide is readily converted into oxygen and carbon monoxide under low pressure electric discharge, and he too calls attention to the analogy between the action of the silent discharge and the action of light in plant life; the polymerizing effects of the silent discharge are especially notable.

The action of this agent is certainly in part electrothermic and, possibly, in part electrolytic, although it is well known that the output of any product secured by means of the silent discharge does not conform to the theoretical yield which would be expected were the reaction governed by Faraday's laws. In the light of our present knowledge it seems most probable that in the silent discharge vast amounts of kinetic energy transformable into chemical energy are introduced into the system by speeding electrons.†

The principal technological application of the silent discharge is the generation of ozone, by the process of Siemens and Halske. A metal tube, cooled by water, is inserted in a tube made of mica which is wound with copper ribbon. The annular space between the two tubes is but narrow, and serves for the passage of the air, the oxygen of which is to be transformed into ozone. The silent discharge passes between the metal cylinder and the copper ribbon on the mica cylinder;

* J. N. Collie, "Syntheses by Means of the Silent Electric Discharge," *Trans. Journ. Chem. Soc.*, London, 1905, p. 1540.

† W. Loeb, *Liber cit.* p. 279.

a series of such double tubes are combined to form a sort of lattice work. An alternating current is employed; about 65 volts are transformed into 6500 volts, and about 18 grams of ozone are produced per electric HP. hour; this amounts to practically nine times the amount which could be secured if this reaction were electrolytic in character.

It is estimated that in the best of ozone-generating plants, not more than 15% of the total energy supplied is consumed in bringing about the transformation of oxygen into ozone.

B. III. **Electro-Osmosis.** — If a porous diaphragm be introduced into an electrolyte and a sufficiently high voltage be employed, the contents of one electrode chamber will be forced bodily through the diaphragm into the other electrode chamber until a certain difference of pressure will have been established between the solutions in the two compartments.

Electro-osmosis, or kataphoresis, as it is also termed, has been known for a long time and was submitted to careful study by G. Wiedemann as early as 1852.* This phenomenon is entirely different from that of osmosis, for in kataphoresis the *whole* solution passes through the diaphragm unchanged, whereas in osmosis only the solvent passes, not the solute. The phenomena of kataphoresis, as recognized by Hittorf, are also independent of electrolytic action and are not subject to the laws of Faraday, although electrolytic phenomena probably accompany the process to a certain extent.

In aqueous solutions, as a rule, the solution travels through the diaphragm from the anode to the cathode compartment, although in certain instances the direction of this flow is reversed; the nature of the solution and the nature of the diaphragm seem to be the determining factors in this matter. The cause of kataphoresis is probably the taking on of oppo-

* G. Bredig, *Ber. des V. Int. Kongresses für Angewandte Chemie*, 1903, Vol. 4, p. 643.

site electric charges by the walls of the diaphragm and by the particles of the solution passing through it.

If no diaphragm is used, but if very finely divided particles of some solid or colloid are suspended in a poorly conducting fluid and an electric current passed through, then the particles of the solid and the particles of the fluid medium in which these are suspended will assume opposite electric charges, and the solid particles will be set in motion. In a general way it may be stated, that substances which, in a finely divided state, take on a charge electronegative to water will travel to the anode; if such substances are made into a diaphragm, they will induce water to travel to the cathode.

An application of kataphoresis — causing a tanning solution to penetrate into and effect the tanning of hides, has resulted in a great saving of time compared with the time required in the former methods of doing this work.

The first attempts in this direction seem to have been made as early as 1850, by Cross; however, his results do not appear to have been very satisfactory. Since that time a considerable number of electro-tanning processes have been devised; in the process of L. A. Groth, in which the hides are kept in motion in a direction at right angles to the electric current passing, it has been found that a treatment of eight hours will give results equivalent to those secured by a full month's tanning according to the old method.

NAME INDEX.

Addicks, 96
Ampere, 17
Arrhenius, 28, 41, 44, 46

Bancroft, 104
Beccaria, 22
Becker, 112
Becquerel, 11, 95
Bémont, 11
Berthelot, 134
Berzelius. 25, 26
Bradley, 128
Bredig, 63, 136
Brodie, 135
Brugnatelli, 25
Bucherer, 112
Buff, 29

Calvert, 45
Carlisle, 24
Cavendish, 22
Clausius, 27, 28, 46
Clifford, 10
Collie, 135
Collins, 32
Cormack, 49
Coulomb, 18
Cowles, 116
Cowper-Coles, 96
Crocker, 34, 128
Crookes, 10, 11
Cross, 137
Cruickshank, 25
Curie, 11
Cuthbertson, 23

Dalton, 26
Davy, 25, 26
De Chalmont, 116
Deimann, 23
De Laplace, 23, 37
Dufaye, 9

Ebert, 14
Elkington, 95

Fabroni, 24
Faraday, 19, 27, 52, 62
FitzGerald, 129, 131
Foerster, 109
Franklin, 9
Fromm, 105

Galvani, 24
Getman, 65
Gilbert, 8
Groth, 137
Grothuss, 25, 27
Guthe, 32

Hall, 112
Hayden, 95
Heimwood, 32
Henry, 20, 24
Héroult, 120
Hess, 37
Hissinger, 25
Hittorf, 63, 64, 136
Hopkins, 47, 60

Jacobi, 103
Jacobs, 129

Jahn, 38
Jordan, 103
Joule, 4, 20

Kahle, 32
Kahlenberg, 58
Keller, 97
Kelvin, 38
Kohlrausch, 32, 33, 60, 62

La Cour, 119
Lavoisier, 3, 23, 37
Le Blanc, 78
Lodge, 44, 65
Loeb, 132, 135
Lorenz, 62
Lovejoy, 128

Marchese, 94
Maxwell, 3
Mayer, 3, 4
Moissan, 116, 123, 124
Murray, 103
Mylius, 105

Nernst, 29, 45, 54, 63, 70
Neuburger, 128
Nicholson, 24

Ohm, 17
Ostwald, 29, 45, 50, 63

Patterson, 32
Planck, 28
Planté, 77
Potter, 117
Priestley, 22

Ramsay, 13
Rayleigh, 32, 33
Richards, 30, 32, 91, 112
Röntgen, 11
Rutherford, 13

Schmidt, 11
Sedgewick, 32
Siemens, 115
Smith, 53
Soddy, 13
Spechnew, 133
Spencer, 103
Stoney, 10
Streintz, 77
Symmer, 9

Taylor, 126
Thomson, 10, 26, 45
Townsend, 127

Van Marum, 22
Van Troostwijk, 23
Van't Hoff, 28, 41, 42, 44
Volta, 17, 23, 24
Von Helmholtz, 28

Walker, 49, 52
Watt, 19
Whetham, 3, 65
Wiedemann, 136
Williamson, 46
Willson, 125
Winkler, 87
Wollaston, 25
Wright, 131

Young, 3

SUBJECT INDEX.

Absolute units, 6, 21
Accumulators, 75, 77, 78
Acetylene gas yield, 126
Acheson furnace, 116
Acheson process, 130
Acid, definition, 50
Acidity, 51
Acker process, 114
Alkali metals, isolation, 25
Alpha-rays, 11
Aluminium, 111
Aluminium production, 112
Alundum, 124
Ammeter, 79
Ampere, definition, 16
Ampere-hour, definition, 18
Anion, definition, 46
Arc furnaces, 115
Aschermann process, 120
Ashcroft process, 102, 114
Atmosphere, electrification, 14

Barium hydrate, 124
Base, definition, 50
Basicity, 51
Bell process, 106, 108
Berzelius' theory, 26
Beta-rays, 12
Betts' process, 100
Borcher's furnace, 117, 121
Browne's process, 101
Bunsen cell, 76

Calcium carbide, 124
Calorie, 20, 38
Capacity factor, 14, 35
Carbides, 124
Carbon bi-sulphide, 126
Carborundum, 130
Carnallite, 113
Castner process, 109, 113
Cathion, definition, 46
Cells, electric, 75, 76
C. G. S. system, 5, 6
Chemical equivalent, 27, 31
Chemical polarization, 74
Chlorates, production, 107
Chlorine and alkali-hydrates, 106
Chromic acid cell, 76
Chromium, 120
Clark cell, 36, 38
Concentration polarization, 73
Conductivity, equivalent, 61
Conductivity, molecular, 60
Conductivity, specific, 62
Conductivity, unit, 59
Constantan, 81
Conductors of electricity, 15
Copper, 94
Copper output calculation, 97
Corundum, artificial, 124
Coulomb, definition, 18
Coulometers, 29, 30
Cross-section of wires, 84
Current amount, calculation, 34

Current density, 74, 87
Current measurement, 79
Current regulation, 81
Current sources, 75

Daniell cell, 38, 76
Davy's electrochemical theory, 26
Deduction, 2
Depolarizers, 68
Diaphragm process, 106, 107
Dielectric constant, 45
Dissociants, 49
Dissociation voltage, 37, 73

Eddy furnace, 118
Edison accumulator, 78
Edison primary cell, 76
Electric arc, temperature, 119
Electric conductors, 15
Electric current, nature, 10
Electric energy, 8, 14
Electric light current, 75, 77
Electric power, calculation, 34
Electric pressure, 16
Electric theory, Berzelius', 26
Electric units, absolute, 21
Electric units, practical, 21
Electric valencies, 46
Electricity, animal, 24
Electricity, contact theory, 24
Electricity, galvanic, 24,
Electricity, nature, 23
Electricity, properties, 14
Electricity, theories, 8
Electro-affinity, 48, 73
Electro-analysis, 66
Electrochemical equivalent, 31, 32, 33
Electrochemical sequence, 47
Electrochemical theory, Davy's, 26
Electrochemistry, evolution, 22
Electrode-areas, calculation, 86
Electrodes, 84
Electrode potential, 74
Electrodeposition from fused electrolytes, 110
Electrodeposition from solution, 94
Electro-furnaces, 114
Electro-furnace products, 119
Electro-organic processes, 132
Electro-osmosis, 156
Electrolyte, 28
Electrolytes, fused, 110
Electrolytic cell, resistance, 83
Electrolytic dissociation, 28, 41
Electrolytic dissociation theory, objections, 58
Electrolysis, 28
Electrolytic solution pressure, 70
Electromotive force, 35, 72
Electron, 8, 10
Electron theory, 10
Electro-plating, 103
Electrotechnology, 93
Electrothermic processes, 114
Electrotyping, 103
Electrozincing, 105
Elements, electrochemical sequence, 47
Energetics, laws, 4
Energy, conservation, 3
Energy, dissipation, 5
Energy efficiency, 92
Energy factors, 4
Energy, forms, 4
Equivalent conductivity, 61
Evolution of electrochemistry, 22

Farad, definition, 19
Faraday, definition, 32
Faraday's laws, 29, 67
Faraday's researches, 27
Forms of energy, 4
Fused electrolytes, 110

Gamma-rays, 12
Gas-equation, 42
General principles of science, 1
Gin furnace, 121
Gin process, 123
Glass, 127
Gold, 99
Goldschmidts' process, 102
Gram equivalent, 31
Graphite, 127
Griesheim—Electron process, 108

Hall aluminium process, 111
Hargreaves and Bird process, 108
Heat equivalent, 20
Heat of formation, 37
Heat summation, 37
Helium, 13
Henry, definition, 20
Heraeus furnace, 118
Héroult aluminium process, 111
Héroult steel process, 120
Hewes process, 126
Hittorf's number, 64
Hoepfner processes, 95, 102, 103
Horse-power, definition, 19
Hydrolysis, 56
Hypochlorites, production, 107
Hypothesis, definition, 2

Indicators, theory, 54
Induction, 2
Induction furnace, 117
Intensity factor, 14, 35
Ion, definition, 45
Ions, existence in electrolytes, 45
Ions, migration, 63
Ions, mobility, 63
Ions, nomenclature, 52
Ion reactions, 50
Ion symbols, 52
Ion theory, 41
Ion-velocity measurement, 65
Ionization, degree, 49
Ionization of water, 51
Ionogen, 53
Iron and steel, 120
Irreversible cells, 69

Jacobs process, 124
Joule, definition, 20
Joule, heat equivalent, 20
Joule's heat, 110
Joule's law, 20, 110

Kataphoresis, 136
Keller furnace, 121
Kellner process, 110
Kilowatt, definition, 19
Kjellin's furnace, 117
Kjellin process, 122

Lamp-bank resistance, 81
Law, definition, 2
Law of heat summation, 37
Lead, 99
Lead accumulator, 77
Length, unit, 5
Litmus, ionization, 56

Machalske process, 129
Magnesium, 113
Manganese, 122
Manganin, 81
Mass, definition, 5
Mass, unit, 5
Matter, conservation, 3
McDonald process, 108
Measurement of physical phenomena, 5
Mercury process, 106, 109
Microfarad, definition, 19
Migration of ions, 63
Mobility of ions, 63
Molecular conductivity, 60
Molybdenum, 122

Nernst lamps, 63
Nernst and Glaser furnace, 118
Neutralization, definition, 51
Nickel, 100
Nickeline, 81
Nitrogen fixation, 128
Nomenclature of ions, 52
Normal current density, 87

Ohm, definition, 17
Ohm's law, 17
One fluid theory, 9
Osmotic pressure, 41, 42
Oxone, 128
Ozone, generation, 135

Part-molecules, 46
Phenol-phthalein, ionization, 55
Phosphorus, 129
Physical phenomena, measurement, 5
Platinoid, 81
Polarization, chemical, 74
Polarization, concentration, 73
Polarization voltage measurement, 75
Pole-papers, 78
Potentiometers, 36
Practical electric units, 21

Radio-activity, 11
Radium, 11, 12, 13
Radium emanations, 13
Rathenau process, 126
Readman and Parker process, 129
Records, 88
Reich process, 127
Resistance boxes, 81
Resistance, definition, 17
Resistance furnaces, 116
Resistance of electrolytic cell, 83
Resumé, 89
Reversible cells, 69
Reversible reactions, 69
Röntgen rays, 10, 12
Roessler and Edelmann process, 103
Ruthenberg process, 122

Salt, definition, 50
Science, general principles, 1
Shade process, 127
Siemens-Halske processes, 94, 99, 101, 102, 135
Silent discharge processes, 133
Silicides, 129
Silicon carbide, 130
Siloxicon, 131
Silver, 98
Simon process, 122
Sodium, 113
Solution pressure, 53
Sources of current, 75
Space, 5
Specific conductivity, 62
Spinthariscope, 11
Substance, conservation, 3
Symbols of ions, 52

Tanning by kataphoresis, 137
Tantalum lamps, 63
Taylor process, 126
Theories of electricity, 8
Thermal energy, 14
Thermopiles, 75, 77
Thomson's theory, 45
Time, definition, 5
Time, unit, 6
Tin, 101
Titanium, 123
Tarnsformer furnace, 117
Tube furnace, 117
Tungsten, 123
Two-fluid theory, 9

Uranium, 123

Vanadium, 123
Voelker furnace, 127
Voltaic pile, 24
Voltameters, 29, 79
Volt, definition, 16
Voltmeter, 36, 79, 80

Water, ionization, 51
Watt-hour, definition, 20
Weber's arc furnace, 122
Weight, definition, 5
Weston cadmium cell, 36
White stuff, 131
Wohwill's process, 99

X rays, 11
Zinc, 102

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